

1051-14-11

Y3 N88:25/4236/41

NUREG/CR-4236

ORNL/TM-9614

Vol. 1

COMPLETED

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Progress in Evaluation of Radionuclide Geochemical Information Developed by DOE High-Level Nuclear Waste Repository Site Projects

ORIGINAL

Report for October-December 1984

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Prepared for the
U.S. Nuclear Regulatory Commission

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PROGRESS IN EVALUATION OF RADIONUCLIDE GEOCHEMICAL INFORMATION
DEVELOPED BY DOE HIGH-LEVEL NUCLEAR WASTE REPOSITORY SITE PROJECTS:
REPORT FOR OCTOBER — DECEMBER 1984

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Manuscript Completed: April 1985
Date Published: October 1985

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NRC FIN No. B0290

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NUREG/CR-3851, Vol. 1
NUREG/CR-3851, Vol. 2
NUREG/CR-3851, Vol. 3
NUREG/CR-3851, Vol. 4

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ABSTRACT

Geochemical information relevant to the retention of radionuclides by candidate high-level nuclear waste geologic repositories being characterized by Department of Energy (DOE) projects is being evaluated by Oak Ridge National Laboratory (ORNL) for the Nuclear Regulatory Commission (NRC). During this report period, emphasis has been given to evaluation of published sorption and solubility information for key radionuclides which is relevant to the Hanford Site in the Columbia River basalts. The removal of neptunium from solution by basalt/groundwater systems under anoxic redox conditions at 60°C proved to be sensitive to the basalt particle size and the test contact time. It was not possible to establish if the neptunium removal from solution was due to sorption or precipitation processes. In studies of uranium solubility, sodium boltwoodite was shown to be the U(VI)-containing phase that precipitates from synthetic groundwater at 60°C. The precipitation of sodium boltwoodite, rather than schoepite which is predicted by geochemical modeling, shows the importance of identifying the solid phase in radionuclide experiments and highlights the weaknesses of the actinide thermodynamic data bases used in geochemical modeling calculations. An evaluation was made of the information developed by DOE on the native copper deposits of Michigan as a natural analog for the possible emplacement of copper canisters in a repository in basalt. The similarity in bulk chemistry of the basalts, relied upon heavily by DOE in their analysis, cannot be used to unequivocally conclude that similar geochemical conditions, and particularly controls on the geochemical conditions, exist within the basalt/water systems at Michigan and at the Hanford Site. Therefore, the DOE analysis is insufficient to conclude, with reasonable assurance, that copper will be stable at the Hanford Site.

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PREFACE

This document is the sixth in a series of progress reports that are being issued by the Nuclear Regulatory Commission to describe the current status of an experimental program to evaluate the radionuclide geochemical information developed by the high-level nuclear waste repository site projects of the Department of Energy.

PROGRESS IN EVALUATION OF RADIONUCLIDE GEOCHEMICAL INFORMATION
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1. EXECUTIVE SUMMARY

This project, supported by the Nuclear Regulatory Commission (NRC), is being conducted to evaluate the radionuclide geochemical information and data acquisition methodology that may be employed by Department of Energy (DOE) high-level nuclear waste repository site projects in performance assessment calculations to show reasonable assurance of expected compliance with regulatory requirements. The project is focused on parameters that are important to the mobility of radionuclides in geologic media (primarily, sorption on host rock and apparent concentration limits in groundwater) under the anticipated geochemical conditions of the repository. Initial emphasis is on information applicable to the Hanford Site candidate repository in the Columbia River basalts on the DOE Hanford Reservation at Richland, Washington, being characterized by the Basalt Waste Isolation Project (BWIP).

Technetium sorption isotherms are being completed under anoxic redox conditions at 60°C for Cohasset basalt/synthetic groundwater GR-4 and McCoy Canyon basalt/synthetic groundwater GR-2 systems. The results will be discussed next quarter after completion of the 50-d batch contact tests.

All of the neptunium solutions used in our work to date are now believed to have contained some portion of neptunium in three valence states: Np(VI), Np(V), and Np(IV). The simultaneous presence of neptunium in three valences, plus the possible hydrolysis and complexed forms of each valence state in groundwater, makes interpretation of experimental sorption or apparent concentration limit results difficult.

A comparison of our results with results published by the BWIP is particularly difficult since BWIP apparently did not investigate the neptunium valence in either the starting solutions or after contact with basalt. We are concerned that failure to adequately consider the possible presence of multiple neptunium valences may represent a deficiency in the BWIP information and could render some of the BWIP sorption results uncertain.

Qualitative observations of our results of anoxic redox condition batch contact experiments at 60°C with Cohasset basalt and synthetic groundwater GR-4 show the following:

1. Removal of neptunium from solution was still occurring after a 60-d contact (i.e., a steady-state condition had not been reached). Sorption ratios as high as 397 L/kg and apparent concentration limits as low as 7.4×10^{-9} mol/L were measured at 60 d.
2. The neptunium sorption ratio measured was highly dependent upon the size of the basalt particles used in the test. Sorption ratios as high as 275 L/kg were measured with <37- μ m-size basalt particles and as low as 4.7 L/kg with a range of <420/>210- μ m-size basalt particles in 14-d experiments.
3. At the present time, we are not able to distinguish between sorption and precipitation processes in the anoxic condition work; either or both processes could be responsible for the removal of neptunium from solution observed in the tests.

Sodium boltwoodite [a U(VI) silicate] was shown to be the U(VI)-containing solid phase that precipitates from synthetic groundwater GR-2 at 60°C. Schoepite is typically assumed to be the stable solid phase in geochemical modeling calculations, partially due to the absence of thermodynamic data for sodium boltwoodite. The unexpected formation of boltwoodite illustrates the importance of identifying the solid phase present in experimental measurements and highlights the limitations of the existing thermodynamic data bases for compounds and conditions of interest to repository assessment. Parallel tests are currently under way with synthetic groundwater GR-4.

An evaluation was made of the information developed by DOE on the native copper deposits of Michigan as a natural analog for the possible emplacement of copper canisters in a repository in basalt. We found that the similarity in bulk chemistry of the basalts, relied upon heavily by DOE in their analysis, cannot be used to unequivocally conclude that similar geochemical conditions (and particularly controls on the geochemical conditions) exist within the basalt/water systems at Michigan and at the Hanford Site. Significant differences exist in the mineralogy and texture of the two basalt occurrences. Better definition of the actual mechanisms involved in controlling the groundwater chemistry is required before a valid analogy can be demonstrated. The DOE analysis did not consider alternative conceptual models for the control of groundwater chemistry. Our evaluation suggests that mechanisms important in the basalt/water system at Michigan may have little relevance to basalt/water interactions at the Hanford Site. For example, interactions between the groundwater, glacial material, and secondary minerals may be the predominant controls in the system at Michigan, whereas basaltic glass/water interactions may be more important for the system at Hanford. The DOE assumptions concerning the "system Eh" of the basalt/water system in Michigan are shown to be incorrect by our evaluation. The system is probably reducing, but precise numerical limits cannot be defined in an unambiguous manner with the available data. Therefore, our evaluation concludes that even though copper probably would be relatively stable in the basalts at the Hanford Site, the DOE analysis is insufficient to demonstrate this stability with reasonable assurance.

2. INTRODUCTION

The objective of this project is to support the NRC staff analysis of geochemical information used by the DOE to predict the performance of candidate high-level waste (HLW) geologic repository sites. Under this project, both experimental and calculational activities are undertaken to evaluate pertinent geochemical values and the methodology used in the development of these values. The results of the work conducted under this project are compared with published information reported by the DOE site projects or others, and (where appropriate) concerns are expressed relative to the accuracy, conservatism, or relevance of the information for the prediction of repository performance.

This project is primarily a laboratory activity because it is anticipated that the DOE may rely on experimentally measured radionuclide apparent concentration limits and sorption distribution coefficients. The experimental methodologies used by the DOE site projects, the selection and characterization of site materials used in the DOE experiments, and the DOE test results are being evaluated. The appropriateness of the materials selected and methodology employed to simulate repository geochemical conditions are considered. The conservatism inherent in the laboratory approach is being evaluated. In addition, attention is directed toward geochemical modeling efforts both to support our laboratory work and to evaluate the data bases and calculational methodologies employed in the geochemical modeling used by the DOE. For example, the DOE site projects may elect to calculate some geochemical values, such as radionuclide solubility, without supporting laboratory measurements.

The DOE site projects may also use modeling methodology to extrapolate laboratory information to conditions of temperature and chemistry that are unexplored experimentally. These and other aspects of the geochemical methodology and values used by the DOE site project will be examined in light of the reasonable assurance criteria of the NRC regulation 10 CFR Part 60.

3. EXPERIMENTAL MATERIALS AND METHODS

All of the test methodology for oxic, reducing, and anoxic redox condition batch contact tests has been described previously (see KERMERS 1985b); the details are not repeated in this report. The preparation and characterization of the basalt samples (KERMERS 1985b) and comparison of the synthetic groundwater formulations (KERMERS 1984c) have also been previously discussed.

4. TECHNETIUM

During this report period, emphasis was placed upon the completion of sorption isotherms for technetium onto basalt under anoxic redox conditions. Previously (KELMERS 1985b), we reported that there was appreciable sorption of technetium onto basalt from solutions with initial pertechnetate concentrations of 10^{-12} , 10^{-8} , and 10^{-6} mol/L, but that the measured sorption ratio (R_s) value was essentially zero at initial pertechnetate concentrations of 10^{-5} and 10^{-4} mol/L. At these higher pertechnetate concentrations, there probably was some technetium sorbed onto the basalt; however, the analytical precision may not have been accurate enough to detect the small differences in solution concentration associated with the sorption. We are, therefore, carrying out additional experiments this quarter at intermediate initial concentrations of pertechnetate to complete the sorption isotherms.

The Hanford Site geochemical systems under evaluation are McCoy Canyon basalt/synthetic groundwater GR-2 and Cohasset basalt/synthetic groundwater GR-4 — both are being studied under anoxic redox conditions at 60°C. During the past quarter, we have completed batch contact experiments for 14-d isotherms for these two systems and have begun experiments for 50-d isotherms. The data for the 14-d experiments are given in Table 1, and the isotherms are plotted in Figs. 1 and 2. Both total technetium and reduced technetium concentrations in solution after contact are given in the table. We did not attempt to determine the valence state of the sorbed technetium. However, it has been shown previously under NRC Project FIN No. B0462 that most of the technetium sorbed on basalt is reduced (MEYER 1985). The reduced technetium in solution was determined by solvent extraction of the TcO_4^- in the centrifuged solution with tetraphenylarsonium chloride in chloroform (MEYER 1985). The isotherms are plotted (Figs. 1 and 2) for both total technetium and reduced technetium in solution vs the sorbed technetium concentration. The isotherms are linear at the lower solution concentrations; however, at the higher concentrations, the shapes suggest a limitation to the ability of the basalt to absorb technetium (apparent sorption capacity). The apparent sorption capacity would depend on the mechanism of sorption. If removal of technetium occurs by reduction by ferrous iron on the surface of the basalt, the limitation could be caused by complete oxidation of all of the surface ferrous iron. On the other hand, removal of technetium occurs by reduction of ferrous ions released from the surface by the basalt followed by subsequent sorption or precipitation of the reduced technetium, then the apparent sorption capacity could depend on a number of kinetic factors such as the surface concentration of ferrous iron or the rates of the processes involved. Other mechanisms could also be involved which would produce apparent sorption capacities. In comparing the data for McCoy Canyon and Cohasset basalts, the values of R_s are a factor of 2 or 3 greater for the Cohasset basalt/GR-4 system than for the McCoy Canyon basalt/GR-2 system. Similarly, the apparent sorption capacity of the Cohasset basalt/groundwater system is larger than that for the McCoy Canyon basalt/groundwater system by a factor of 2 or 3. For both systems, the

concentrations of reduced technetium in solution in the linear region of the isotherms were about 20% of the total technetium concentrations in solution.

After the completion of the parallel 50-d experiments, the results will be discussed in more detail and put in perspective with published information for the Hanford Site.

Table 1. Technetium sorption by basalt under anoxic redox conditions at 60°C^a

Initial TcO ₄ ⁻ (mol/L)	Final pH	R _s (L/kg)	Final concentration of Tc (mol/L) ^b	
			Total	Reduced
McCoy Canyon basalt, synthetic groundwater GR-2, 14-d contact:				
3 x 10 ⁻¹²	9.0 ^c	3.5 ± 0.2	(2.1 ± 0.1) x 10 ⁻¹²	3.9 x 10 ⁻¹³
1 x 10 ⁻⁸	9.1	5.5 ± 0.8	(6.6 ± 0.3) x 10 ⁻⁹	1.9 x 10 ⁻⁹
5 x 10 ⁻⁷	9.5	5.0 ± 2.3	(3.4 ± 0.3) x 10 ⁻⁷	3.3 x 10 ⁻⁸
1 x 10 ⁻⁶	9.0	4.0 ± 0.1	(7.2 ± 0.2) x 10 ⁻⁷	3.5 x 10 ⁻⁸
2 x 10 ⁻⁶	9.5	2.0 ± 0.2	(1.7 ± 0.1) x 10 ⁻⁶	6.4 x 10 ⁻⁸
5 x 10 ⁻⁶	9.5	1.1 ± 0.1	(4.5 ± 0.1) x 10 ⁻⁶	4.3 x 10 ⁻⁸
1 x 10 ⁻⁵	9.5	0.5 ± 0.1	(9.5 ± 0.1) x 10 ⁻⁶	4.7 x 10 ⁻⁸
Cohasset basalt, synthetic groundwater GR-4, 14-d contact:				
1 x 10 ⁻¹²	8.5	12.1 ± 2.7	(5.6 ± 0.5) x 10 ⁻¹³	1.2 x 10 ⁻¹³
1 x 10 ⁻⁸	8.5	16.2 ± 1.1	(3.6 ± 0.1) x 10 ⁻⁹	8.1 x 10 ⁻¹⁰
5 x 10 ⁻⁷	8.6	13.0 ± 0.5	(2.1 ± 0.1) x 10 ⁻⁷	2.8 x 10 ⁻⁸
1 x 10 ⁻⁶	8.5	9.8 ± 0.7	(4.8 ± 0.1) x 10 ⁻⁷	3.7 x 10 ⁻⁸
2 x 10 ⁻⁶	8.6	9.0 ± 5.1	(1.1 ± 2.6) x 10 ⁻⁶	4.8 x 10 ⁻⁸
5 x 10 ⁻⁶	8.6	3.1 ± 0.3	(3.8 ± 0.1) x 10 ⁻⁶	6.1 x 10 ⁻⁸
1 x 10 ⁻⁵	8.6	2.0 ± 0.5	(8.3 ± 0.4) x 10 ⁻⁶	9.0 x 10 ⁻⁸

^aExperimental conditions: anoxic environment, -70/+325 mesh-size basalt crushed and stored under argon, contacted for 14 d at 60°C; solution recovered after contact by centrifugation at 5000 rcf under argon. About 0.4 g basalt and 4 mL groundwater spiked with ⁹⁹TcO₄⁻ and traced with ^{95m}TcO₄⁻ were used.

^bValues of R_s and total solution concentration are averages of three determinations. No standard deviations are shown for reduced technetium concentration because only one solution from each set was tested for reduced technetium.

^cTwo different sets of data were used to complete this isotherm. Those done in this quarter have a final pH of 9.5, and those done earlier have final pH values of 9.0 and 9.1. For unknown reasons, the starting pHs of the two different batches of groundwater were different. Normally, the pH drops during the runs, in this case from 0.3 to 0.4 pH unit for all of the runs. Hence, the final pH values fall into two different sets.

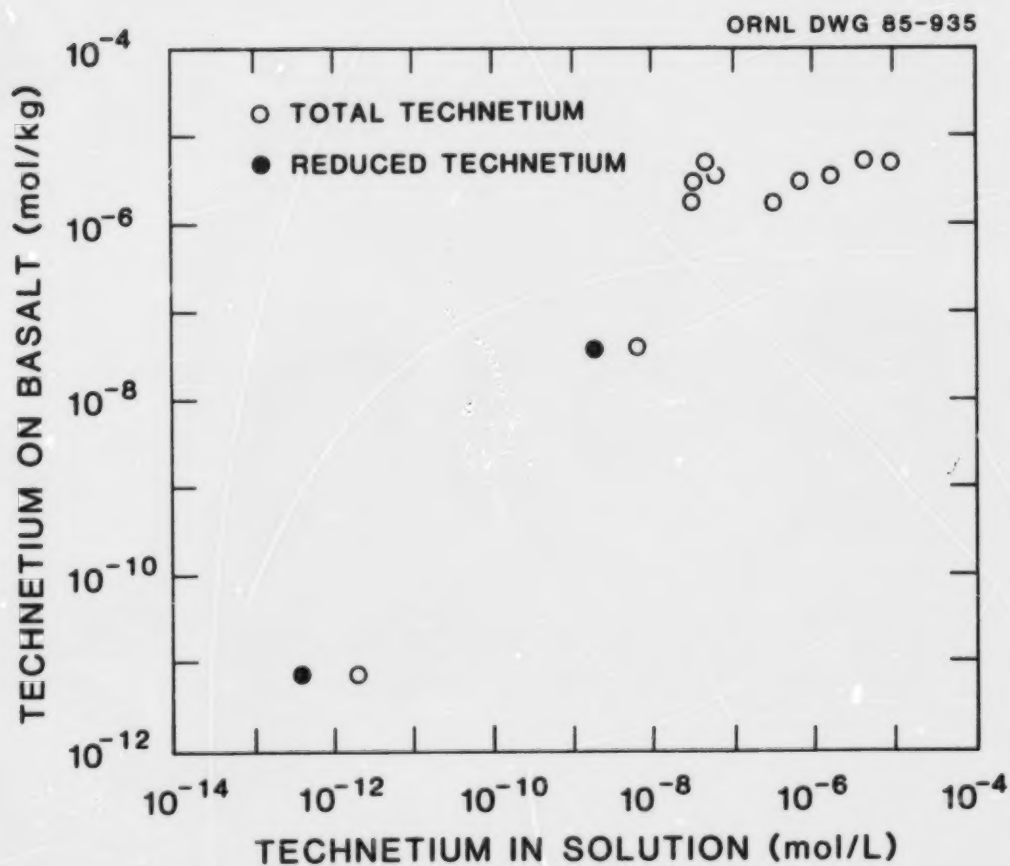


Fig. 1. Sorption of Tc on McCoy Canyon basalt from GR-2; anoxic condition, 14 d, 60°C.

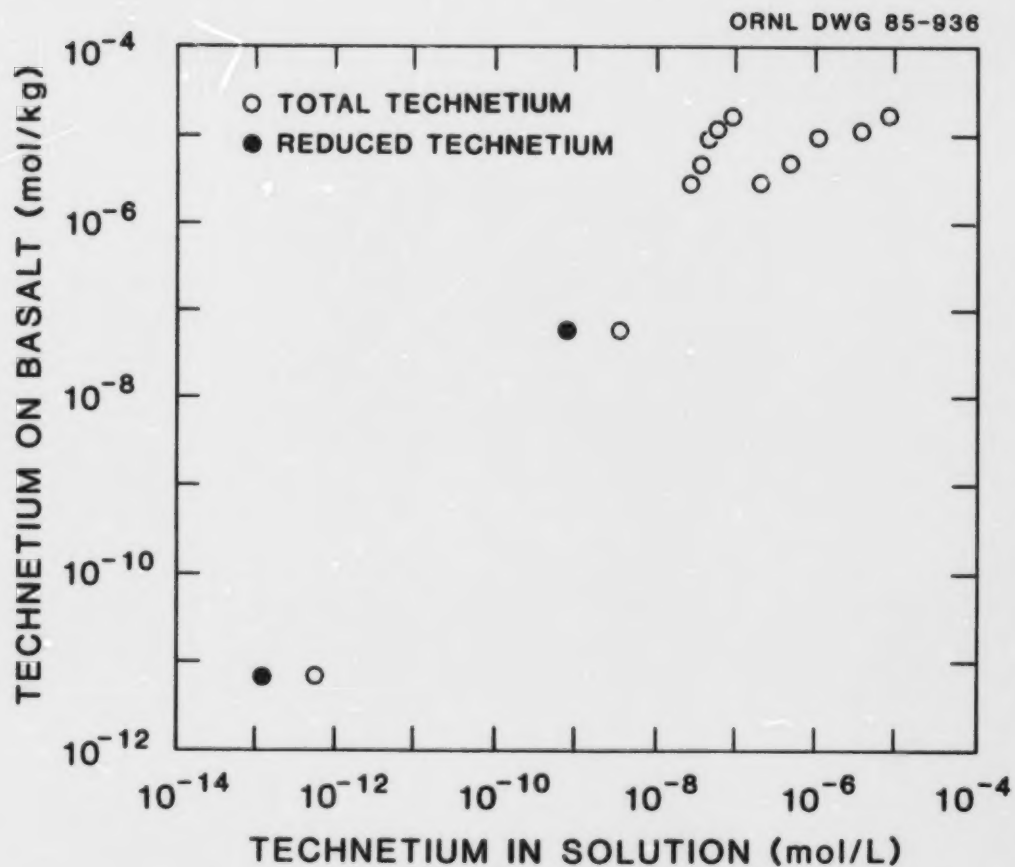


Fig. 2. Sorption of Tc on Cohasset basalt from GR-4; anoxic condition, 14 d, 60°C.

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5. NEPTUNIUM

5.1 RESULTS AND DISCUSSION

5.1.1 Effect of Contact Time

A series of tests was conducted under anoxic redox conditions to measure the effect of contact time on the sorption of neptunium from synthetic groundwater GR-4 onto Cohasset basalt in batch contact experiments at 60°C. Contact periods of 1 to 60 d were employed. The neptunium valence state, as well as the total neptunium concentration in solution before and after contact, was determined. The neptunium-spiked GR-4 initially contained primarily (>80%) Np(V), but some Np(IV) and Np(VI) were also present. The concentration of Np(IV) in solution after contact was surprising, since it shows a higher solubility than previously reported for Np(IV) hydrous oxide (RAI 1985). The results (Table 2 and Fig. 3) suggest that Np(V) and Np(VI) in solution may be first reduced to Np(IV) by the basalt/groundwater system and the Np(IV), then removed from solution by sorption or precipitation reactions at a slower rate (perhaps formation of hydrous oxides). However, this removal from solution could also involve initially the rapid sorption of some Np(V) and Np(VI) species, followed by slower reduction to and sorption of Np(IV). This can best be seen in Fig. 3, where the curves representing Np(VI) and Np(V) concentrations initially drop more rapidly with time than the total neptunium concentration curve. A steady-state condition had not been achieved in 60 d (the longest contact time tested); removal of a small but significant percentage of neptunium from the solution was still continuing between the 32- and 60-d experiments. Earlier work with Umtanum basalt and Np(V)-spiked GR-2 synthetic groundwater (MEYER 1985) has shown steady-state sorption conditions within 7 to 14 d. These differences in attainment of a steady-state condition are unexplained at this time.

Much of our earlier neptunium sorption work with McCoy Canyon basalt under oxic redox conditions employed contact times of either 7 or 28 d (KELMERS 1984b, KELMERS 1984c, KELMERS 1985b). In those tests, little difference was observed in the 7- or 28-d sorption ratios (other test parameters held constant); that is, a steady-state condition was apparently reached in <7 d. Many of the results published by the BWIP for oxic or reducing redox conditions with samples from several different basalt flows employed contact times of 50 to 65 d (SALTER 1981). The effect of contact time on neptunium sorption was not discussed in that reference. If the chemisorption reactions believed (KELMERS 1985b, MEYER 1985) to be involved in the reduction and sorption of neptunium by basalt under anoxic redox conditions are not rapid, the test contact time would be an important experimental parameter. A further experimental complexity exists since the "Np(V)" solutions used in our work are now known to contain some Np(IV) and Np(VI) as well as Np(V) (KELMERS 1985b). Redox reactions involving the three neptunium valence states might not all be rapid and could result in slow changes in the sorption

ratio (or precipitation) with experimental contact time. The work published by the BWIP did not report neptunium valence analyses. The limited laboratory work that we have completed to study the effect of contact time, in combination with the chemical complexity of the neptunium/groundwater solutions, does not permit a quantitative understanding of the sorption reactions involved, but does reveal the sensitivity of the measured sorption ratio to the test contact time under anoxic redox conditions.

Table 2. Effect of contact time on neptunium sorption^a

Contact time (d)	R _s (L/kg) ^c	Final concentration (mol/L) ^c	Percentage of initial	Neptunium in solution			
				Valence (%)			
				(IV)	(V)	(VI)	MB ^b
0d		(3.0 ± 0.1) × 10 ⁻⁷	100	13.2	81.9	3.8	98.9
1	23 ± 1	(9.0 ± 0.2) × 10 ⁻⁸	30	38.6	55.6	4.8	99.0
2	38 ± 5	(6.3 ± 0.8) × 10 ⁻⁸	21	59.1	32.3	8.4	99.8
8	53 ± 8	(4.8 ± 0.7) × 10 ⁻⁸	16	64.4	34.7	2.0	101.1
16	113 ± 18	(2.4 ± 0.4) × 10 ⁻⁸	8	66.8	33.9	2.2	102.9
32	147 ± 9	(1.9 ± 0.1) × 10 ⁻⁸	6.3	69.7	34.1	3.2	107.0
60	397 ± 91	(7.4 ± 1.7) × 10 ⁻⁹	2.5	68.8	33.2	1.8	103.8

^aTest conditions: 0.4 g of Cohasset basalt (-70/+325 mesh) contacted with 4.0 mL of synthetic GR-4 groundwater containing 3 × 10⁻⁷ mol/L ²³⁷Np and traced with ²³⁵Np under anoxic conditions at 60°C; solution recovered by centrifugation for 20 min at 5000 rcf. The neptunium valence distribution was determined with one of the three aqueous samples from each time-period test.

^bMB = material balance; total of ²³⁵Np counts in the three valence solutions divided by the initial ²³⁵Np counts.

^cMean ± 1 standard deviation for triplicate tests.

^dNo basalt present.

5.1.2 Effect of Particle Size

A series of neptunium sorption tests was conducted to explore the effect of the particle size (and associated variation in surface area) of the basalt used in the tests. The particle size of the basalt samples used in sorption studies reported in Salter (1981) was 30 to 850 μm, while a basalt particle-size range of 44 to 210 μm had been used in most of the previous work with McCoy Canyon basalt on this project. Our size-effect tests were conducted with Cohasset basalt fractions ranging from <410/>210- to <37-μm-size particles under anoxic conditions at 60°C for 14 d.

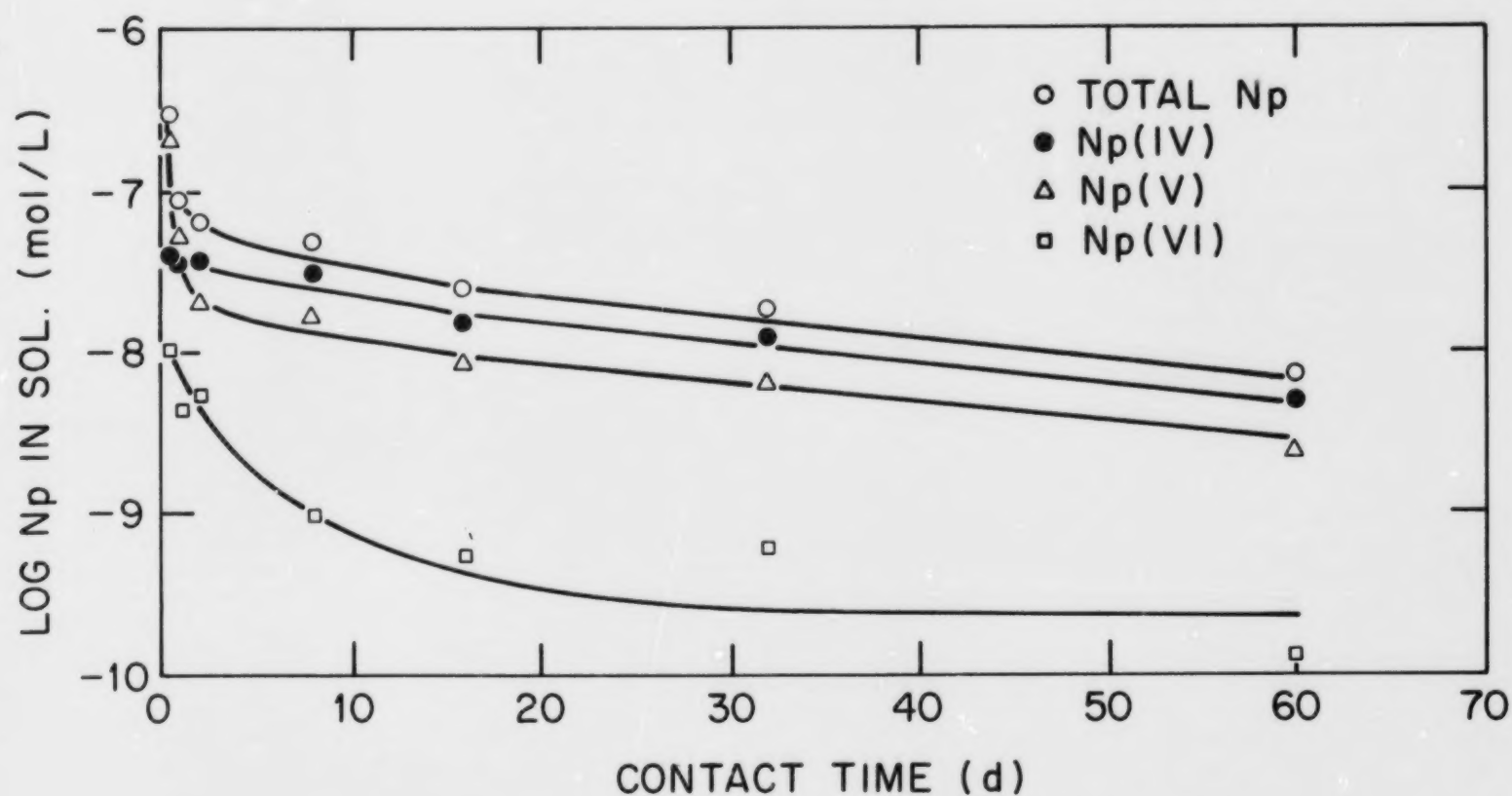


Fig. 3. Effect of contact time on the sorption of neptunium by Cohasset basalt from GR-4 synthetic groundwater.

The neptunium sorption ratio value (R_s) increased significantly (from 4.7 ± 1.2 to 275 ± 134 L/kg) with decreasing basalt particle size (Table 3 and Fig. 4). In Fig. 4, the vertical error bars indicate the standard deviation for the R_s value while the horizontal bars indicate the particle-size range of the sample used in the test. The results thus appear as rectangles in the figure. If an R_s value is calculated based on a weighted average of the three particle-size fractions used in the preceding anoxic condition rate tests ($-70/+325$ mesh), a calculated sorption ratio of ~ 100 L/kg is obtained. This amount is close to the value of 113 ± 18 L/kg obtained at 16 d (Table 2).

The valence of the neptunium after contact with the various particle-size fractions of basalt was determined (Table 3). Before contact, most of the neptunium was present as $Np(V)$ (Table 2, zero time point); after contact the dominant valence was $Np(IV)$. Some portion of all three neptunium valence states were present in all samples. Little change was noted in the $Np(VI)/(V)/(IV)$ distribution evident in Table 3 for the tests with different particle-size fractions of basalt.

These initial results clearly demonstrate the importance of the basalt sample particle size on the sorption ratios measured by batch contact methodology, and suggest that caution should be taken in comparing test results obtained with samples of differing particle sizes. Since we now believe that the neptunium removal-from-solution phenomenon results from chemisorption reduction reactions, possibly involving $Fe(II)$ atoms on the basalt surface, the increased sorption resulting from finer-sized basalt fractions may reflect the greater surface area present with the finer particles. Scanning electron micrographs (Fig. 5) did not indicate any classification of specific minerals into some size fractions, thus, there is no evidence to suggest that the effect of basalt size on the R_s value resulted from enrichment of a unique, strongly sorptive basalt phase in the finer fractions. Because both increased contact time and reduced particle size result in greater neptunium sorption, it is possible that both parameters could be resulting in increased availability of $Fe(II)$ for the reductive chemisorption reaction(s).

5.2 CONCLUSIONS

The following conclusions are drawn from this work:

1. All the neptunium solutions used in our experimental work to date are now believed to have contained some proportion of neptunium in three valences: $Np(VI)$, $Np(V)$, and $Np(IV)$. Under oxic redox conditions, the solutions are primarily $Np(V)$; unfortunately, in our earlier oxic redox condition work we did not determine neptunium valence states. Under anoxic redox conditions in the presence of basalt, the neptunium seems to be primarily reduced to $Np(IV)$; with time, although, some $Np(V)$ and $Np(VI)$ persist in solution. The simultaneous presence of neptunium in three valence states, plus the

Table 3. Effect of particle size on neptunium sorption^a

Particle size (μm)	Mesh size	R_s^b (L/kg)	Neptunium after contact			
			Final concentration ^b (mol/L) ^c	Valence (%)		
				(IV)	(V)	(VI)
<420/>210	-40/+70	4.7 $\pm$ 1.4	(12.1 $\pm$ 0.7) $\times 10^{-8}$	69.6	22.6	7.8
<210/>105	-70/+140	14.5 $\pm$ 6.0	(8.6 $\pm$ 1.5) $\times 10^{-8}$	70.3	15.5	6.8
<105/>74	-140/+200	56.6 $\pm$ 10.8	(4.0 $\pm$ 0.6) $\times 10^{-8}$	52.5	21.6	6.6
<74/>44	-200/+325	202.0 $\pm$ 142	(1.7 $\pm$ 1.1) $\times 10^{-8}$	65.0	24.0	1.9
<44/>37	-325/+400	235.0 $\pm$ 104	(1.2 $\pm$ 0.5) $\times 10^{-8}$	65.3	24.3	13.0
<37	-400	275.0 $\pm$ 168	(1.5 $\pm$ 1.3) $\times 10^{-8}$	73.5	18.5	16.7

^aTest conditions: 0.4 g of Cohasset basalt contacted with 4.0 mL of synthetic groundwater GR-4 spiked with 3×10^{-7} mol/L ^{237}Np and traced with ^{235}Np . Contact time of 14 d under anoxic conditions at 60°C.

^bMean value $\pm$ standard deviation for three determinations.

^cThese percentages were computed from the count rate and the volumes of the solutions used in the extractions. They do not sum to 100% because of counting statistics, errors in determination of the small volumes, and losses of Np, probably on test tube surfaces.

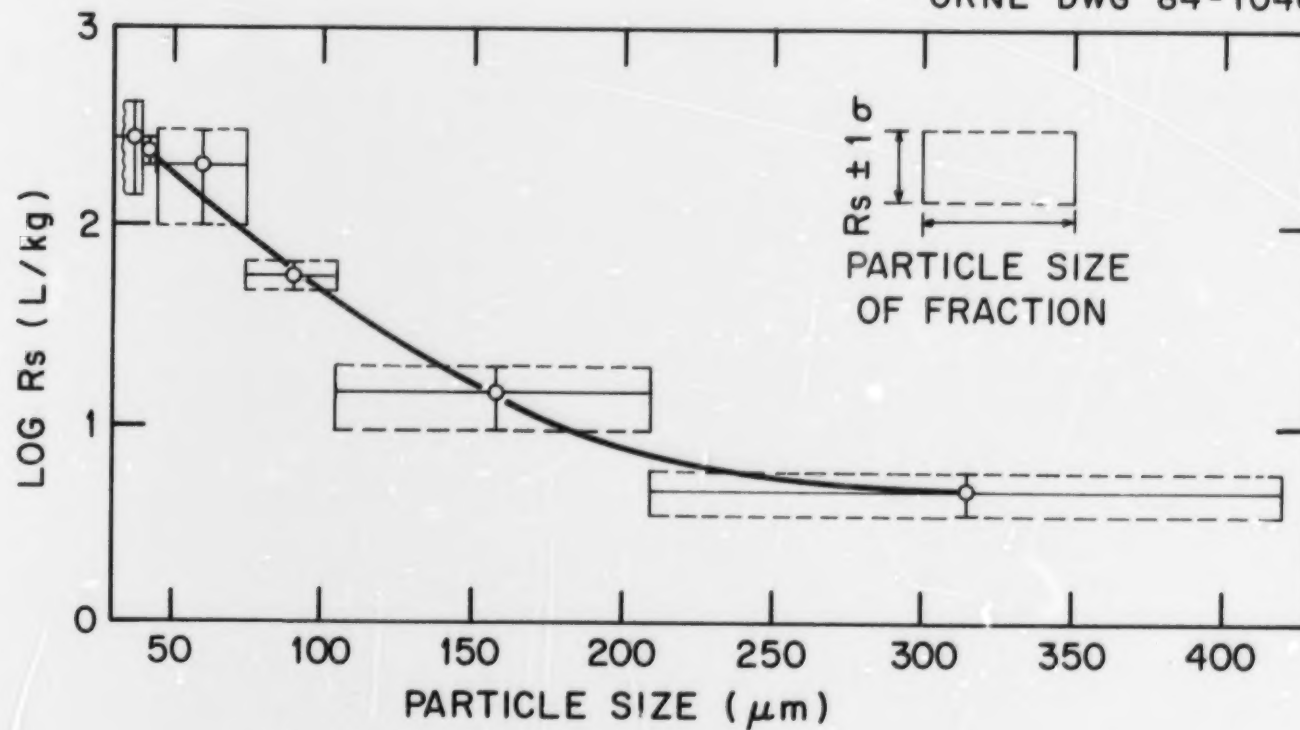
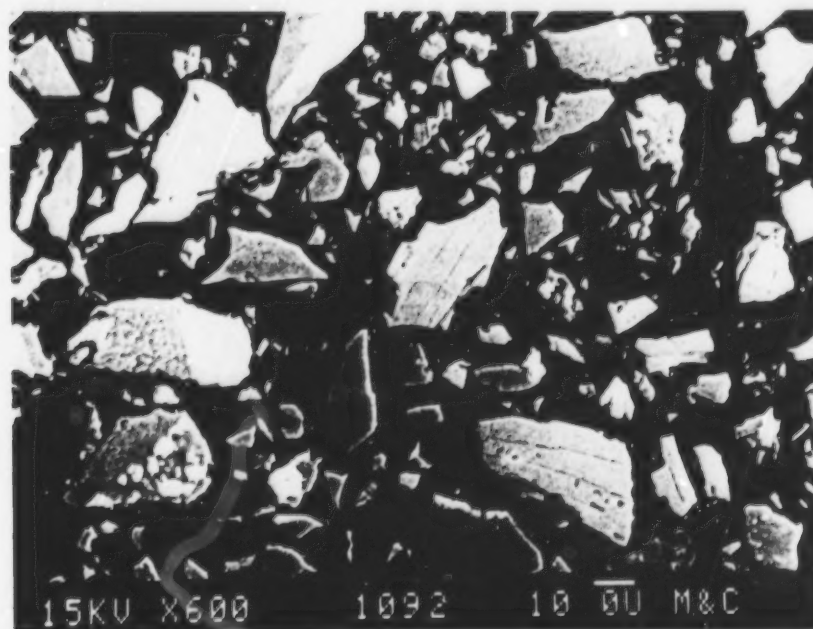
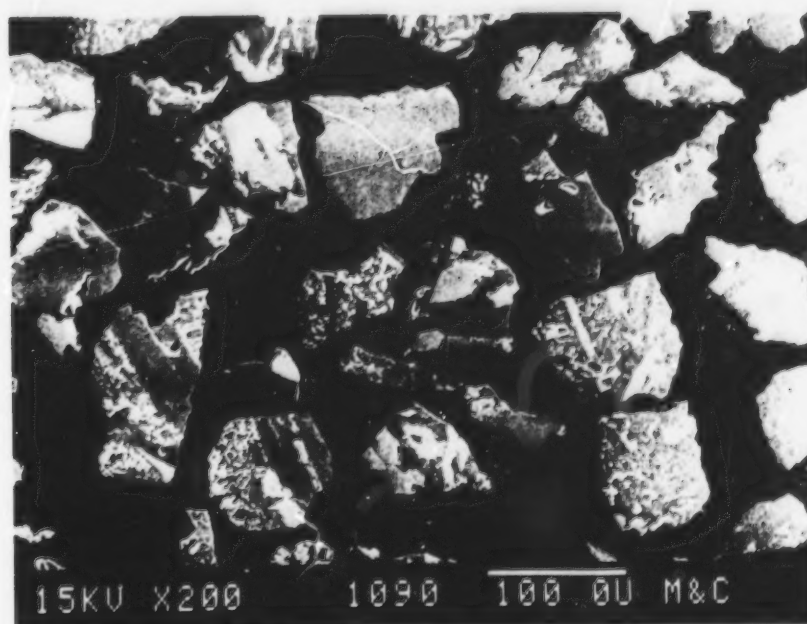


Fig. 4. Effect of particle size of Cohasset basalt on the sorption of neptunium from GR-4 synthetic groundwater. Particle size of smallest fraction was <37 μm.

14



(a)



(b)

Fig. 5. Scanning electron micrographs of (a) -400 mesh and (b) -140/+200 mesh Cohasset basalt.

possible existence of hydrolyzed and complexed forms of each neptunium valence state, makes a quantitative interpretation of experimental sorption or apparent concentration limit results difficult. Since the neptunium sorption work published by the BWIP did not identify the neptunium valence state(s) present in either starting solutions or after contact with basalt, it is not possible to directly compare our results with their work.

2. Under anoxic redox conditions in tests with Cohasset basalt and synthetic groundwater GR-4 at 60°C, removal of neptunium from solution by sorption and/or precipitation reactions was still continuing after 60 d (i.e., a steady-state condition had not been reached). Sorption ratios as high as 397 L/kg and solution concentrations as low as 7.4×10^{-9} mol/L neptunium were measured.
3. Under anoxic redox conditions with Cohasset basalt and synthetic groundwater GR-4 at 60°C, the neptunium sorption ratio was highly dependent upon the particle size of the basalt used in the experiment. Sorption ratios as high as 275 L/kg were measured with <37- μ m-size basalt particles.
4. The limited work which we have completed during this report period under anoxic conditions does not permit a distinction between neptunium precipitation or sorption processes. Either, or both, processes could be involved in the chemisorption reduction reactions causing the removal-from-solution phenomenon observed in our experiments.

5.3 EVALUATION OF PUBLISHED SORPTION AND SOLUBILITY INFORMATION

A variety of neptunium solubility values have been published by the BWIP (Table 4). In general, experimentally observed or calculated solubility values for Np(V) under oxidizing conditions have ranged from 10^{-5} to 10^{-7} mol/L. Much lower solubility values have been calculated for NpO₂ under the reducing conditions expected by the BWIP in the repository; these values have ranged from 10^{-10} to 10^{-20} mol/L. The most recent report, the Draft Environmental Assessment (DEA 1984), gives a solubility value range of 10^{-7} to 10^{-9} mol/L for ²³⁷Np (DEA 1984, Table 6-27). (It is not clear why only one specific isotope of neptunium was identified.) An earlier report (SALTER 1983) gave "expected" and "conservative" neptunium solubility values of 10^{-10} and 10^{-5} mol/L, respectively, for use in performance assessment calculations.

A variety of neptunium sorption or distribution coefficient values have been reported by the BWIP (Table 5). In general, values obtained under oxidizing conditions have been low to moderate, ~4 to ~40 L/kg, but much higher values (200 to ~1000 L/kg) were reported under reducing conditions (hydrazine present).

Our previous work under oxidizing conditions with McCoy Canyon basalt and synthetic groundwater GR-2 gave an average neptunium sorption ratio

of 1.7 L/kg. We expressed concern that the measured or expected distribution coefficient values, and even the conservative value for neptunium of 2 L/kg (SALTER 1983, DEA 1984), might not only be too high (i.e., nonconservative), but inaccurate (KELMERS 1984c, KELMERS 1984d, KELMERS 1985b). Our work under anoxic redox conditions with Cohasset basalt and synthetic groundwater GR-4 described in this report has yielded much higher neptunium sorption ratios. With contact times as long as 60 d or basalt particles as fine as $<37 \mu\text{m}$, sorption ratios of 275 to 397 L/kg were obtained. These values are higher than the reducing condition value of 200 L/kg given in the Site Characterization Report (SCR 1982), but are lower than the value of 1015 L/kg initially reported in Salter (1981) for reducing conditions (hydrazine present). Our anoxic condition values are much higher than the expected or conservative values for performance assessment calculations of 2 or 10 L/kg (SALTER 1983, DEA 1984).

In evaluating the conservatism or accuracy of the experimentally derived data for use in performance assessment radioactivity release calculations, an important unresolved question exists concerning the suitability of the batch contact experimental methodology to model in situ radionuclide behavior. In both our laboratory work and that published by the BWIP, crushed basalt particles were used in the experiments. Thus, radionuclide sorption may be construed as occurring primarily on fresh basalt surfaces in these experiments. Reactions between fresh basalt surfaces and synthetic groundwater may control the test geochemical conditions and the measured apparent concentration limit values. If the backfill in the Hanford Site engineered facility is primarily crushed basalt, then these batch contact experiments may model radionuclide behavior in the engineered facility; however, the experiments have not been run at the elevated temperatures of up to 250°C — conditions that may exist in some portions of the backfill after repository closure. Groundwater migration in the far field, however, may be occurring primarily through existing fractures and the permeable basalt flow top(s). Fractures and flow top voids are known to be lined with secondary minerals (calcite, smectite, zeolites, etc.), and these secondary mineral linings may substantially inhibit the interaction of radionuclides in migrating groundwater with the basalt primary minerals. In any case, freshly exposed basalt surfaces would not be present. Thus, it is not completely certain that the current batch contact experimental methodology adequately models radionuclide behavior.

Table 4. Neptunium solubility values published by the BWIP

Reference	Neptunium (mol/L)	Comments
SALTER 1981	$\sim 1 \times 10^{-5}$ $\sim 1 \times 10^{-18}$ to 1×10^{-20}	Oxidizing conditions Repository conditions
EARLY 1982, EARLY 1984	9×10^{-9}	Eh = -0.3 V
SCR 1982	2×10^{-7} 1×10^{-18}	Oxidizing Reducing
SALTER 1983	1×10^{-10} 1×10^{-5}	"Expected" "Conservative"
DEA 1984	1×10^{-7} to 3×10^{-9}	For ^{237}Np

Table 5. Neptunium sorption values published by the BWIP

Reference	Kd (L/kg)	Comment
SALTER 1981	4.1 ± 0.9 30 ± 13 42 ± 11 1015 ± 164	Flow E basalt, 23°C, oxidizing Umtanum, 23°C, oxidizing Umtanum, 60°C, oxidizing Umtanum, 60°C, reducing (hydrazine)
SCR 1982	10 200	Basalt, oxidizing, "conservative best estimate" Basalt, reducing, "conservative best estimate"
SALTER 1983	10 20 10 2	Umtanum, oxidizing, measured Umtanum, reducing, measured "Expected" "Conservative"
DEA 1984	2 to 10	For ^{237}Np

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6. URANIUM

6.1 RESULTS AND DISCUSSION

We have previously reported (KELMERS 1985a) the formation of a light-yellow-colored precipitate in blank tests (no basalt present) from initial concentrations of 10^{-4} mol/L uranyl chloride in synthetic groundwaters at 60°C under both oxic and anoxic redox conditions. We could not tell if the precipitate also formed in parallel tests in the presence of basalt since the presence of the basalt particles obscured any precipitate that may have formed. We have repeated the blank experiments on a larger scale to prepare enough precipitate for x-ray diffraction (XRD) analysis. The procedure used for this preparation was as follows:

About 0.3 g of $^{238}\text{UO}_3$ was dissolved in water containing stoichiometric HCl and evaporated to dryness. The resulting solid uranyl chloride was twice dissolved in water and evaporated to dryness. A stock solution of ^{238}U uranyl chloride in water was prepared from the solid. Freshly prepared synthetic groundwater GR-2 (500 mL) was brought to 10^{-4} mol/L U(VI) by the addition of portions of this stock solution. The groundwater was then traced by the addition of 2.9×10^4 dpm/mL of ^{233}U uranyl chloride in 0.01 mol/L HCl. The groundwater was transferred to two 250-mL bottles and placed into a controlled-atmosphere glove box containing argon. The samples were then agitated for 24 d at 60°C. After they were removed, a light-yellow precipitate was observed in the bottles. The solution had lost over 90% of the ^{233}U counts (counted in an aliquot recovered by centrifugation). The solid was recovered by centrifugation at 600 rcf in the controlled-atmosphere glove box. For XRD analysis, a capillary tube was loaded with the wet precipitate in an argon atmosphere by ORNL Analytical Chemistry Division personnel.

The precipitate was identified as sodium boltwoodite, $\text{Na}(\text{UO}_2)(\text{SiO}_3)(\text{OH}) \cdot 5/2\text{H}_2\text{O}$, by powder XRD techniques (Card No. 13-215, Powder Diffraction File, Joint Committee on Powder Diffraction Standards). The uranium concentration in the solution above the precipitate was 7.5×10^{-6} mol/L, as determined by counting the ^{233}U . In order to examine the formation of this compound under other conditions, we are extending the study of uranium sorption isotherms under anoxic conditions to include blanks of uranyl chloride in synthetic groundwater GR-4 and again are looking for the formation of a precipitate. These experiments are under way and will be described in future reports.

6.2 CONCLUSIONS

Sodium boltwoodite precipitated at 60°C from synthetic groundwater GR-2 containing U(VI); the apparent concentration limit observed was 7.5×10^{-6} mol/L.

6.3 EVALUATION OF PUBLISHED SORPTION AND SOLUBILITY INFORMATION

The formation of sodium boltwoodite, rather than schoepite, as the stable solid phase shows the importance of identifying the solid phase present in experimental measurements and highlights the limitations of the existing thermodynamic data bases for compounds and conditions of interest to repository assessment. We have noted previously (KELMERS 1985b) that we are observing concentration limits for uranium that are lower than the calculated solubility value of 10^{-4} mol/L reported in the Site Characterization Plan (SCR 1982) for oxic conditions. Lower values for reduced uranium species were reported by Early (1982). In the absence of basalt, we saw no evidence of uranium reduction under anoxic conditions. For the experiment reported here, the apparent concentration limit was 7.5×10^{-6} mol/L for sodium boltwoodite. Because of lack of thermodynamic data, sodium boltwoodite is not included in the data bases for PHREEQE (PARKHURST 1980), MINTEQ (FELMY 1984), or EQ3/EQ6 (WOLERY 1983). Therefore, calculation of U(VI) solubility limits in systems with significant quantities of silica, such as synthetic groundwaters GR-3 or GR-4, would tend to overestimate the concentration of uranium.

7. GEOCHEMICAL MODELING

7.1 INTRODUCTION

Crisman and Jacobs (1982) studied the native copper deposits (~500 million years old) in the Portage Lake Volcanics near Hancock, Michigan, as a natural analog for the emplacement of copper canisters in the proposed HLW repository in the basalts at the Hanford Site, Washington. Although copper is not currently a leading candidate material for the containment canister of HLW or spent fuel, its inherent stability under some natural conditions makes it desirable to maintain copper as an option (BIRD 1982), especially if it can be shown that the geochemical conditions in a repository may encompass the thermodynamic stability field of native copper.

Crisman and Jacobs (1982) argued for significant similarity between the geochemical conditions, and the processes controlling them, in the basalt/groundwater system in Michigan and those in the deep basalts at the Hanford Site, Washington. We have evaluated the work of Crisman and Jacobs to determine whether there is a valid analogy between the basalt/water systems of Michigan and Washington, and if the data and interpretations of Crisman and Jacobs provide an adequate basis for reasoning by analogy that copper will have favorable corrosion characteristics in the deep basalts at the Hanford Site. Our evaluation assessed the quality of the data and considered alternative conceptual models for the interpretation of the data. This was done in order to determine the validity of the analogy and the conclusions drawn from it pertaining to the potential performance of copper as a canister material.

7.2 DOE METHODOLOGY AND INFORMATION

Crisman and Jacobs (1982) collected samples of basalt and groundwaters from the Michigan Technology University Mining Laboratory (MTUML) in order to compare them with those of the Hanford Site, Washington. The purpose of the comparison was to determine whether significant similarity exists between the two systems. Then, by analogy to the existence of native copper in the basalts of Michigan for over 500 million years, it could be reasoned that copper may be stable (or at least alter only slowly) in the basalt/groundwater system at the Hanford Site, Washington. To establish that the analogy was valid, Crisman and Jacobs attempted to show that similar geochemical conditions exist in the two basalt/groundwater systems. Near-surface groundwaters were collected that seep through a sequence of the Portage Lake Volcanics (a copper-bearing basalt unit) in an adit of the MTUML. Changes in the water chemistry were evaluated as a function of depth into the adit (i.e., increasing overburden) and flow rate, and the chemistry of the waters were modeled using WATEQF (PLUMMER 1976). Combining these relationships with published information on the mineralogy and chemistry of the basalts, Crisman and Jacobs suggested that the basalt effectively controls the chemistry of these groundwaters as they flow through the basalt (~10 to 100 m in thickness).

The primary conclusions of Crisman and Jacobs (1982) included:

1. Native copper, precipitated from hydrothermal solutions at elevated temperatures, has undergone little alteration while in contact with both saline and fresh groundwaters for over 500 million years.
2. The basalt in the MTUML has maintained the necessary geochemical conditions through rapid equilibration with groundwaters to allow the copper to remain essentially unaltered for over 500 million years. Furthermore, the chemistry of near-surface groundwaters reflects this control of water chemistry by the basalt.
3. Enough similarity exists between the basalt/groundwater system in Michigan and that at the Hanford Site in Washington to reason, by analogy, that copper may be stable in the basalt/groundwater system at Hanford and, thus, may be a potentially favorable material for the long-term containment of HLW and spent fuel.

7.3 EVALUATION OF DOE INFORMATION

In order to evaluate the work of Crisman and Jacobs (1982), the following activities were completed: (1) an assessment of the information reported (CRISMAN 1982) (including data and interpretations), (2) a check on the reported calculations by modeling the groundwater chemistry with the geochemical computer code MINTeq (FELMY 1984), (3) an analysis of the groundwater chemistry as a function of estimated equilibration time with the basalt in the MTUML, and (4) an analysis of the state of redox equilibrium and possible controls on the redox conditions in the groundwater.

7.3.1 Basalt Mineralogy and Chemistry

Crisman and Jacobs (1982) compare the mineralogy and chemistry of the Portage Lake Volcanics to that of the Umtanum flow of the Grande Ronde Basalt at the Hanford Site. At the time of the study, the Umtanum flow was the reference horizon for a repository. Currently three other flows are also being considered: Rocky Coulee, McCoy Canyon, and Cohasset (presently the leading candidate). Although a detailed evaluation should be accomplished before any final conclusions are drawn, differences in the mineralogy and chemistry among these four candidate flows are not likely to be great enough to invalidate conclusions extrapolated from one flow to another for the purpose of such natural analog studies.

Crisman and Jacobs (1982) do not report any detailed characterization of the samples of basalt collected from the MTUML. Rather, published information on the mineralogy and chemistry of the Portage Lake Volcanics is utilized. The samples collected were apparently only used to confirm the similarity of the general mineralogic nature of the Portage Lake Volcanics in the MTUML and the basalts discussed in the literature referenced by Crisman and Jacobs.

Crisman and Jacobs (1982) conclude that, despite major differences in the mineralogy and texture between the basalts in Michigan and those of the Hanford Site, the similarity of the bulk chemistry (CRISMAN 1982, Table 5) establishes a good basis for reasoning by analogy. Crisman and Jacobs state that:

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Acknowledging that overall mechanisms and details of the chemistry may be different, it is probable that, based on bulk rock chemistry, controls on the groundwater chemistry in the two geohydrologic systems would be similar.

The above statement is one of the premises on which many of the conclusions of Crisman and Jacobs (1982) were based and, therefore, should be considered in some detail.

The chemistry of groundwaters can be influenced by:

1. the original source and nature of the water,
2. rock/water interactions, and
3. the nature and character of groundwater flow and dilution.

Reactions that generally control, or at least contribute to, the chemical composition and speciation of waters include: precipitation, dissolution, hydrolysis, complexation, ion exchange, adsorption, and oxidation/reduction. Given that (1) and (3) above are fixed for a given rock/water system, it is the interaction of groundwater with specific phases of a rock which will predominantly influence the chemistry of the groundwater. Using thermodynamic arguments, one would predict that two rock/water systems of identical bulk chemical composition, under identical physicochemical conditions, would evolve to the same equilibrium state regardless of the phases present initially. However, this situation rarely occurs in groundwater systems because kinetics generally dominate the behavior of low-temperature rock/water systems. Therefore, the initial mineralogy and texture of a rock can significantly affect the chemical characteristics of groundwater in contact with the rock. For example, two rock/water systems may consist of an identical quantity of silica, but if one rock contains quartz as the silica phase and the other contains amorphous silica, it is likely, based on kinetic arguments (RIMSTIDT 1981), that the groundwaters present in the two systems would contain different quantities of dissolved silica (higher dissolved silica in the system with amorphous silica). As another example, two rock/water systems may contain significantly different quantities of total calcium, but if both systems have calcite present as the only calcium-bearing phase accessible to the groundwater, it is likely that the dissolved calcium content of the groundwaters in both systems would be identical (assuming all other parameters are held constant). Therefore, even though the bulk chemical composition may be similar, because the Portage Lake Volcanics and the basalts at Hanford are vastly different in their texture and mineralogy, the conclusion of Crisman and Jacobs (see above) would appear to be of questionable validity.

Rock/water interactions may not be the sole contributor to the chemistry of groundwaters; therefore, it is important to consider other processes. For example, it has been suggested that the sodium-chlorine-type groundwaters in the Grande Ronde Basalt at the Hanford Site may originate by the mixing of shallow groundwaters (Na-HCO₃ type) with saline groundwater from a deeper source, rather than result from rock/water interactions

(EARLY 1984b). This hypothesis is supported by results from high-temperature rock/water interaction tests (APTED 1982), in which sodium and chlorine are found to behave as conservative elements. These data conflict with the synthesis of Crisman and Jacobs (1982) which associates increasing sodium-chlorine contents with increasing reaction of water and rock for the systems in Michigan and at the Hanford Site.

7.3.2 Groundwater Chemistry

Crisman and Jacobs (1982) collected samples of near-surface groundwater seeping into the MTUML through thicknesses of basalt ranging from a few meters to ~100 m. The samples were analyzed for major element chemistry, pH, and alkalinity (see Table 6). The following chemical relationships were reported for the groundwaters of the MTUML as a function of distance into the adit (i.e., increasing overburden): increasing concentrations of sodium and chlorine, decreasing concentrations of calcium and HCO_3 , and increasing pH. Crisman and Jacobs compare these relationships with the apparent systematic changes in water chemistry (Na, Ca, Cl, and HCO_3) as a function of depth at the Hanford Site (GEPHART 1979). Crisman and Jacobs modeled the chemistry of the groundwaters from the MTUML with the geochemical code WATEQF (PLUMMER 1976) and identified several possible mineralogical solubility controls. Because of the probable short equilibration time between the Portage Lake Volcanics and the near-surface groundwaters (maximum overburden is approximately 90 m), it was concluded that the Portage Lake Volcanics effectively control the groundwater chemistry through rock/water interactions, and that, in an analogous manner, the Grande Ronde basalt may control the chemistry of deep groundwaters at the Hanford Site. Crisman and Jacobs state that:

...given sufficient time for equilibration, the near-surface waters of the Pewabic Amygdaloid may approach, in gross characteristics, the waters of the Grande Ronde Formation, even though the actual mechanisms of control may be somewhat different.

From this premise, Crisman and Jacobs (1982) then conclude that, because native copper has been stable in the Portage Lake Volcanics for approximately 500 million years, copper may be relatively stable (or at least alter only slowly) in the basalts at the Hanford Site because geochemical conditions similar to those in the Michigan basalt/water system may be present. Crisman and Jacobs recognize that the controls on the groundwater chemistry may not be identical, but go on to suggest that enough similarity exists to make the analogy valid.

As Crisman and Jacobs (1982) discuss, pH and redox conditions are probably the primary variables affecting the stability of copper in groundwaters. However, Crisman and Jacobs do not directly address the redox conditions in the basalt/water system in Michigan. Rather, this issue is only indirectly addressed through an analysis of the coexisting mineral phases: native copper and hematite. Crisman and Jacobs conclude (in a somewhat circular manner) that the Portage Lake Volcanics control the redox conditions within a range encompassing the stability of native copper. They apparently assume that, because the chemistry of the basalt/water systems

Table 6. Characteristics and chemistry of water samples from MTU Mining Laboratory adit

Sample No.	QW-3	QW-4	QW-5	QW-6	QW-7	QW-8	QW-9	QW-10a	QW-10b	QW-11a	QW-11b
Date	10/30/81	10/30/81	10/30/81	10/30/81	10/30/81	10/30/81	11/02/81	11/02/81	11/07/81	11/02/81	11/07/81
Position, ^a m	354	315	282	229	110	44	15	c	c	d	d
Flow rate, ^b L/min	2.4×10^{-2}	6.5×10^{-3}	1.2×10^{-2}	1.4×10^{-1}	4.7×10^{-2}	2.7×10^{-1}	4.0×10^{-1}	c	c	d	d
Sample T, °C	8.5	9.0	9.0	8.5	11.0	11.0	11.0	7.0	7.5	9.0	9.5
pH (at T °C)	8.91(22)	8.76(22)	8.65(22)	7.98(22)	8.70(22)	8.05(22)	7.69(19.5)	7.1(17)	7.1(19)	7.55(18)	7.61(20)
Concentration (mg/L)											
Na	57.8	55.4	70.8	23.9	38.5	7.75	14.9	32.6	31.5	20.6	21.4
K	<0.3	<0.3	<0.3	1.05	<0.3	<0.3	0.809	2.99	3.29	2.02	2.06
Ca	3.36	3.30	3.63	23.5	10.5	36.1	35.9	33.9	33.0	28.6	30.1
Mg	0.267	0.236	0.259	3.66	2.04	5.15	7.23	5.58	5.81	5.29	5.53
Sr	0.021	0.027	0.022	0.102	0.063	0.120	0.127	0.187	0.157	0.125	0.130
Cu	<0.006	0.022	0.008	<0.006	0.011	<0.120	0.040	0.604 ^e	0.021	0.029	<0.006
Fe	0.111	0.106	0.078	<0.006	0.035	0.068	0.036	0.132	0.108	0.048	0.021
Mn	0.004	0.004	<0.003	<0.003	<0.003	0.069 ^e	0.005	<0.003	<0.003	0.007	<0.003
Al	0.167	0.164	0.12	<0.075	0.095	0.087	0.141	0.175	0.091	0.473 ^e	0.099
B	1.98	2.63	2.77	0.21	0.18	0.064	0.155	0.288	0.294	0.220	0.231
SiO ₂	15.4	17.5	19.5	13.2	14.2	14.5	13.	10.3	10.6	11.4	12.1
HCO ₃	81.5	74.6	77.2	83.8	83.5	108.	110.	106.	103.	84.6	84.6
Cl	27.	20.	46.	12.	12.	3.	13.	41.	40.	31.	27.
NO ₃	5.	4.	2.	8.	3.	f	1.	5.	4.	8.	1.
SO ₄	13.	13.	12.	13.	12.	7. ^e	12.	16.	16.	14.	14.
F	0.9	0.07	0.07	0.03	0.04	0.02	0.03	0.04	0.03	0.03	0.03

^aRelative distance into adit from entrance.^bNormalized to 1 m².^cSurface stream in glacial material, north of entrance to adit.^dWaterfall over basalt ledge, ~15 m above entrance to adit.^eApparent outlier with respect to other data.^fDetected, not quantitative.

SOURCE: CRISMAN 1982. D. P. Crisman and G. K. Jacobs, Native Copper Deposits of the Portage Lake Volcanics, Michigan: Their Implications with Respect to Canister Stability for Nuclear Waste Isolation in the Columbia River Basalts Beneath the Hanford Site, Washington, RHO-BW-ST-26P, Rockwell Hanford Operations, Richland, Washington, 1982.

in Michigan and at the Hanford Site is similar, the redox conditions in the basalt/water system at the Hanford Site will also encompass the stability field for native copper.

The following sections will address two important aspects of the study by Crisman and Jacobs (1982) that may have some impact on the conclusions relevant to the controls on groundwater chemistry. First, the sample collection and characterization procedures will be evaluated. These procedures directly affect the quality and usefulness of the data and, therefore, the conclusions. Second, an evaluation of the interpretations pertaining to mechanisms controlling the chemistry of the groundwaters will be discussed. Our evaluation includes some confirmatory geochemical modeling to check the calculations of Crisman and Jacobs, as well as consideration of some alternative conceptual models which may be used to interpret the data.

7.3.2.1 Sample Collection and Characterization

Crisman and Jacobs (1982) collected water from drip sites on the roof of the MTUML adit into plastic bottles that were then sealed. The samples were brought to a laboratory for filtering, acidification, and pH and alkalinity determinations. The time lapse from sample collection to the determination of pH and alkalinity was ~4 h. As seen in Table 6, the temperatures of the samples during this time increased approximately 10°C (compare sample temperature to temperature at pH determination). The increase in temperature probably resulted in some change in speciation and possibly CO₂ degassing. As a result of these changes, the pH and alkalinity values reported for the samples are probably not representative of the in situ values. This difference should not affect an analysis of relative differences among the samples, but certainly makes any conclusions pertaining to characteristics dependent on pH and alkalinity (e.g., calcite saturation indices) uncertain and difficult to validate.

Crisman and Jacobs (1982) do not report uncertainties with the analytical determinations of the concentrations of major elements. It is difficult to evaluate the validity of conclusions regarding absolute, or relative, differences in the chemistry of the samples without having some estimate of the possible range of a given value. In addition, there are analytical determinations that appear to be outliers with respect to the data (see Table 6). Crisman and Jacobs do not address this potential problem and do not discuss whether these outliers were used in the analysis of solubility controls and geochemical relationships. For our evaluation, these outliers were not included in the analysis of geochemical trends for the element of interest or the calculation of saturation indices for a phase involving the element. Crisman and Jacobs do not discuss how maximum concentrations (see "< values" in Table 6) were treated. In our evaluation, these maximum values were assumed to represent the actual concentration in the analysis of geochemical trends as well as in the calculation of saturation indices.

In the discussion of physiographic characteristics around the MTUML, Crisman and Jacobs (1982) do not document the depth or characteristics of the glacial material overlying the basalt sequence. This information

is important because clays, which are common in some glacial deposits, can significantly influence the chemistry of groundwaters in contact with them. Without information on the extent and chemical/mineralogical characteristics of the glacial material, it is difficult to establish the relative importance of the basalt versus the glacial material in controlling the chemistry of the groundwaters seeping into the MTUML. Therefore, the validity of the analogy between the rock/water systems in Michigan and Washington cannot be demonstrated conclusively.

7.3.2.2 Data Interpretation

Geochemical Modeling: The groundwater analyses of Crisman and Jacobs (1982), as shown in Table 6, were modeled with the geochemical code MINTEQ (FELMY 1984) to verify their calculations. The calculated saturation indices ($SI = \log AP/K$, AP = ion activity product, K = equilibrium solubility product) agreed, in general, with those of Crisman and Jacobs. The permissible solubility controls identified by Crisman and Jacobs of chalcedony (for silicon) and calcite (for calcium), phases reported to be present in the Portage Lake Volcanics, were confirmed. Crisman and Jacobs identified albite as a possible control on sodium. With MINTEQ, all samples were calculated to be slightly oversaturated with respect to this phase — probably a result of slightly different thermodynamic data in the two geochemical models. As was determined by Crisman and Jacobs, no viable permissible solubility control for magnesium could be identified.

Because of the uncertainty associated with pH and alkalinity determinations of Crisman and Jacobs (1982) (see Sect. 7.3.2.1), the results of geochemical-model calculations may bear little relevance to the in situ mechanisms involved in controlling the groundwater chemistry. For example, if the pH and alkalinity are systematically in error, then saturation indices calculated for calcite would also be systematically in error — thus, a result of $SI = 0.0$ for calcite would be fortuitous. Therefore, the identification of permissible solubility controls is uncertain, and the relative differences between samples should be given more emphasis.

Geochemical Trends: In order to assess some alternative interpretations of the groundwater chemistry, two evaluations were accomplished. First, the mechanism of ion exchange for controlling the concentrations of sodium and calcium was assessed by analyzing the trends of milliequivalents of Na, K, Mg, and Ca. Second, the relative contact time (t^*) between the groundwater and the rocks above the MTUML was estimated in order to evaluate geochemical trends as a function of time. From this information, it is possible to qualitatively assess the importance of solubility constraints in controlling the chemistry of the groundwaters. For example, the concentration of selected elements in the surface waters, which should start out undersaturated with respect to most phases, would be expected to increase more slowly during transport through the basalt overburden above the MTUML if dissolution/solubility mechanisms are involved, rather than ion exchange, which, in general, is a more rapid process. Also, coupled effects on the behavior of one element by another may be investigated.

As Crisman and Jacobs (1982) discuss, the flow of the near-surface groundwaters above the MTUML will be predominantly through fractures (CRISMAN 1982, Fig. 13). Because of a lack of actual hydrologic data, and in order

to simplify the analysis of equilibration times, it was assumed that the basalt is fractured enough so that porous media behavior is applicable and that Darcy's Law may be applied. (This assumption may be totally invalid, but it is necessitated by a lack of hydrological data.) No hydrologic data are reported for the rocks in the immediate vicinity of the MTUML, except for the flow rates measured by Crisman and Jacobs at the drip sites. Therefore, for the purpose of this evaluation, it was assumed that the groundwater flows through rocks above the MTUML that possess identical and homogeneous hydrologic characteristics except for the distance of the flow paths. This distance was measured from the cross section showing sample locations [CRISMAN 1982 (Fig. 10), after BUMGARNER 1980]. Crisman and Jacobs report flow rates normalized to 1 m^2 . Therefore, with the stated assumption above, the flow rate of each sample can be defined as the relative Darcy velocity of the water through a column of rock of height "h" and a cross-sectional area of 1 m^2 . These velocities are then normalized to the lowest flow rate. The relative contact time (t^*) for each sample is then calculated by dividing the overburden by the normalized velocity. A summary of this approach and the results of the calculations are listed in Table 7. An important limitation of this analysis is that the extent and characteristics of the glacial material overlying the basalt are not known. Therefore, as discussed in Sect. 7.3.2.1, the relative influence of the glacial material and the basalt on the chemistry of the groundwaters cannot be explicitly established. An arbitrary relative contact time of zero was assigned to the four samples of surface waters (see Table 7).

Figure 6(a) illustrates the relationship between milliequivalents of Na + K and Ca + Mg for the water samples of Table 6. If ion exchange were the only mechanism involved in controlling the chemistry of these elements, the data would approximate a straight line of slope -1.0 [see dashed line of Fig. 6(a)]. The data, with more samples occurring below the dashed line, do not fit this relationship perfectly. However, the close approximation to a linear relationship with a slope near -1.0 suggests that ion exchange may be the dominant mechanism controlling the concentration of these elements. This interpretation is in contradiction to the conclusion of Crisman and Jacobs, who suggest that solubility constraints of calcite and albite control the concentrations of calcium and sodium, respectively. The near mirror-like relationship between Na + K and Ca + Mg shown in Fig. 6(b) supports the interpretation of ion exchange as an important mechanism. The surface waters ($t^* = 0$) are initially rapidly depleted in Na + K, with a subsequent gradual increase in concentration with increasing t^* . This relationship suggests that the glacial material may impart an initial signature on the groundwater, which is then altered with increasing contact time with the basalt.

Figure 7 illustrates that ion exchange may also play an important role in controlling the concentration of strontium in the waters by analogy with the behavior of calcium and magnesium — an interpretation consistent with the similar ionic properties of the elements and the fact that the waters are calculated to be undersaturated with respect to strontium-bearing phases. Figure 7 also illustrates that potassium, much lower in concentration than sodium, is apparently removed rapidly from the surface waters with increasing t^* , rather than behaving like sodium, which increases in concentration. This pattern is consistent with the typical behavior of potassium (HEM 1970).

Table 7. Overburden, normalized velocity, and relative contact time for sample locations in the MTUML

Sample No.	Overburden (m)	Normalized velocity (m/t*)	Relative contact time ^a (t*)
QW-3	89	3.7	24.1
QW-4	81	1.0	81.0
QW-5	75	1.8	41.7
QW-6	72	21.5	3.3
QW-7	44	7.2	6.1
QW-8	15	41.5	0.4
QW-9	7	61.5	0.1
QW-10a and QW-10b ^b	0		
QW-11a and QW-11b ^c	0		

^aCalculation of relative contact time (t*):

Assume hydrologically homogenous columns of basalt, height h = overburden and area $A = 1 \text{ m}^2$ for each sample location.

Assume Darcy's Law is applicable:

$$Q = Av$$

Q = flow rate, m^3/min
 A = area, m^2
 v = Darcy velocity, m/min

Because $A = 1 \text{ m}^2$, define $Q = v$;

Normalize velocity (v^*) to lowest flow rate (Q_{QW-4}), see Table 6:

$$v^* = Q/Q_{QW-4}$$

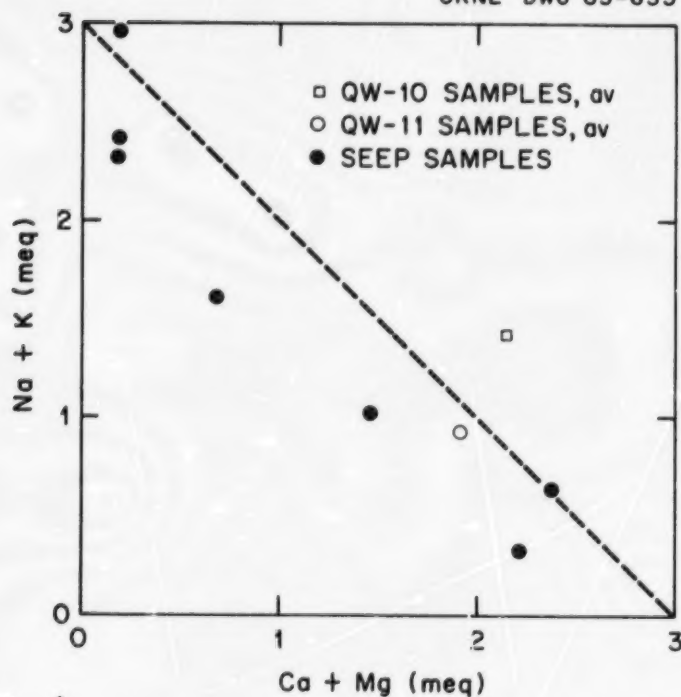
Relative contact time (t^*) is then calculated from:

$$t^* = h/v^*$$

^bSurface stream north of adit in glacial material.

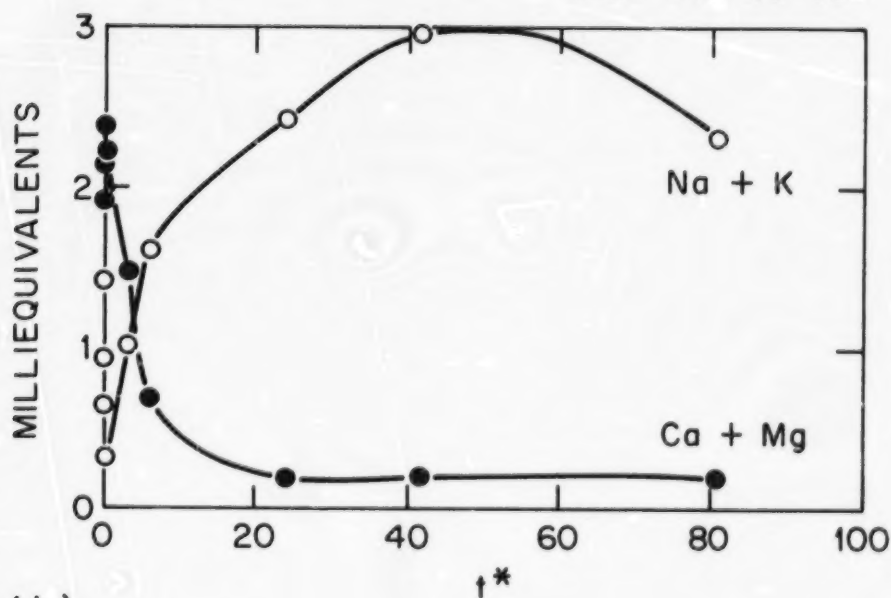
^cWaterfall over a basalt ledge ~15 m above entrance to adit.

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(a)

ORNL DWG 85-634



(b)

Fig. 6. (a) Milliequivalents of Na + K versus Ca + Mg for water samples listed in Table 6. (b) Na + K and Ca + Mg versus t^* (relative contact time) for water samples of Table 6.

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Figure 8 illustrates the relationship of pH, total carbonate, and silica as a function of t^* . Recognizing the limitations in the measured pH values (see Sect. 7.3.2.1), the relative changes in pH as a result of increased contact time are dramatic. The pH rises from initial values of 7.1 and 7.6 (see samples QW-10 and QW-11) to an apparent "steady-state" value of ~8.8 (average of four seep samples with highest pH values). Total carbonate decreases rapidly from an initial value for the seep samples of ~1.8 mmol/L to a value of 1.4 mmol/L, and then decreases only gradually thereafter. Silica increases gradually with increasing t^* and may be approaching an apparent steady-state value, although the data are not sufficient to conclusively demonstrate this steady-state behavior. The relationship between the saturation index for chalcedony and t^* (Fig. 9) supports the hypothesis of an approach to steady state for silica. The waters are initially calculated to be undersaturated with respect to chalcedony, but as the contact time increases, the waters are calculated to become saturated with respect to chalcedony. However, Deutsch et al. (1982) suggest that calculated saturation indices within $\pm 5\%$ of the log K value for that phase should be considered to be at saturation. All the saturation indices for chalcedony fall within this uncertainty band, suggesting that the pattern as a function of t^* could be fortuitous. Although the trends of saturation index with t^* suggest that definite changes are occurring with time, and support the conclusion of Crisman and Jacobs that the basalt may be an effective control on the chemistry of the groundwaters, the data do not allow an unequivocal interpretation at this time.

To further investigate possible controls on the concentration of calcium, saturation indices for calcite were plotted versus t^* (Fig. 9).

According to the $\pm 5\%$ of log K criterion for saturation, all samples are saturated with calcite. However, as with silica, the trend with increasing t^* suggests that systematic changes in water chemistry are occurring. The surface water samples are calculated to be undersaturated with respect to calcite. The groundwaters are calculated to rapidly saturate and eventually become undersaturated (perhaps reaching a steady-state value) with increased contact time.

This behavior is consistent with the changes observed for calcium, total carbonate, and pH. A mechanism of calcium removal by ion exchange (Fig. 6) coupled with solubility control by calcite will result in an increase in pH and a decrease in total carbonate (Figs. 7 and 8). The decreases in calcium and total carbonate are not stoichiometric (~0.75 mmol and ~0.56 mmol, respectively). Thus, to maintain calcite saturation, an increase in pH from an independent mechanism is required (e.g., hydrolysis of silicates). The increase in silica concentration (see Fig. 8) supports the possibility of this mechanism. The apparent steady-state pH (see Fig. 8) appears to be a result of rock/water reactions (calcite solubility control and silicate hydrolysis) and not a result of solution buffers. The geochemical relationships for calcium, sodium, total carbonate, and silica can be consistently explained with this mechanism, although the uncertainty associated with the pH and alkalinity determinations must be kept in mind (see Sect. 7.3.2.1).

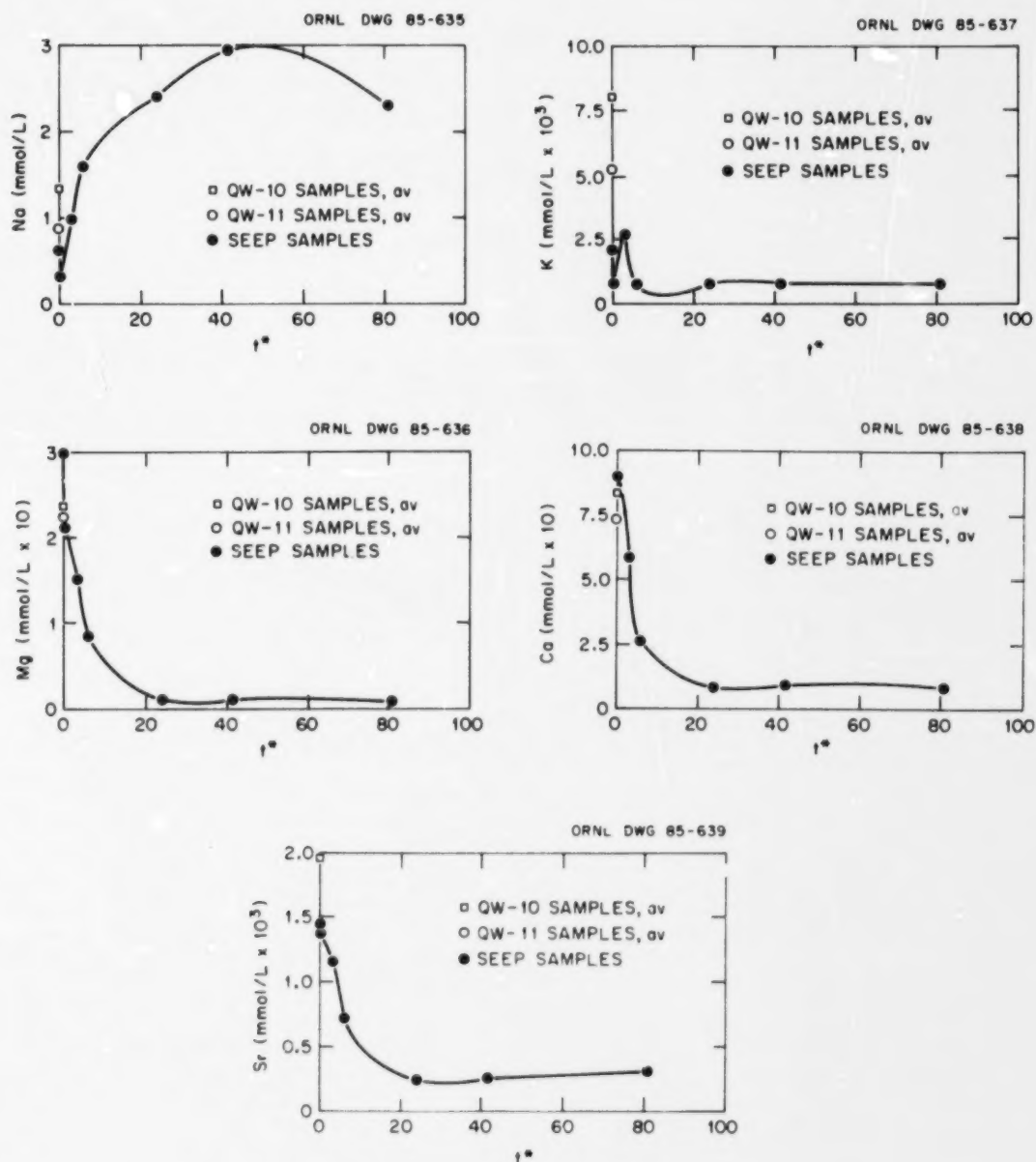


Fig. 7. Concentration versus t^* (relative contact time) for selected elements of water samples listed in Table 6.

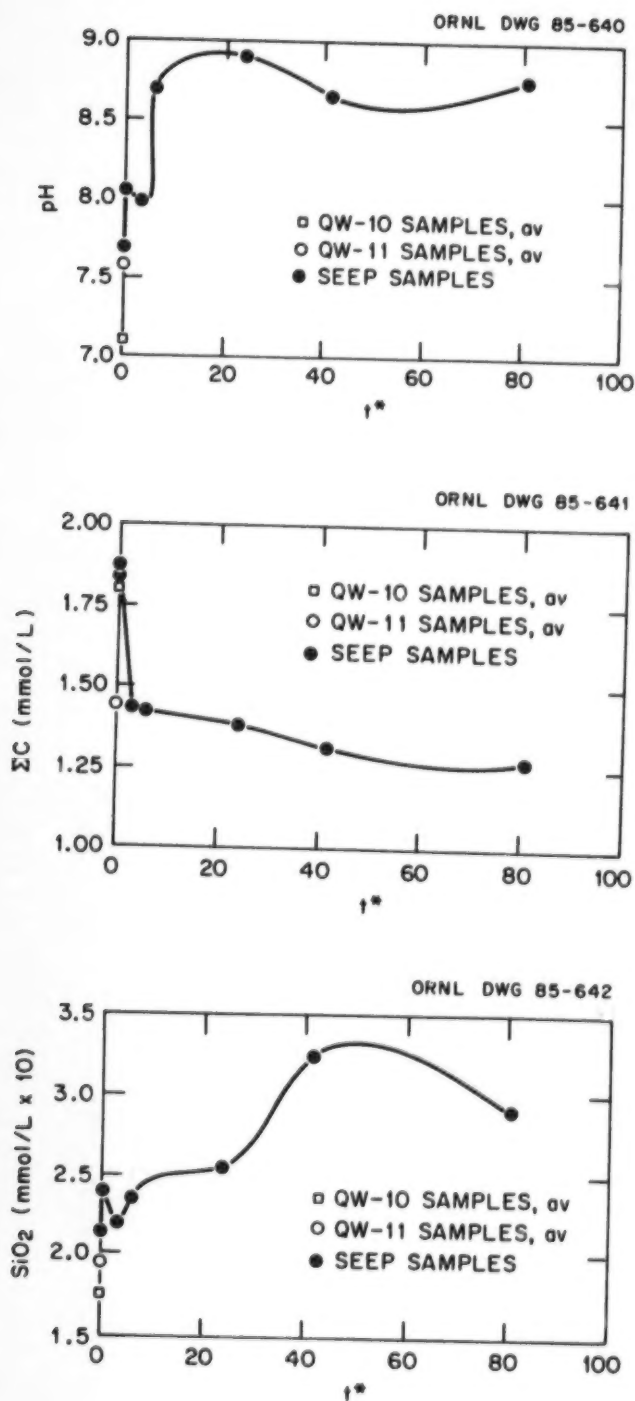
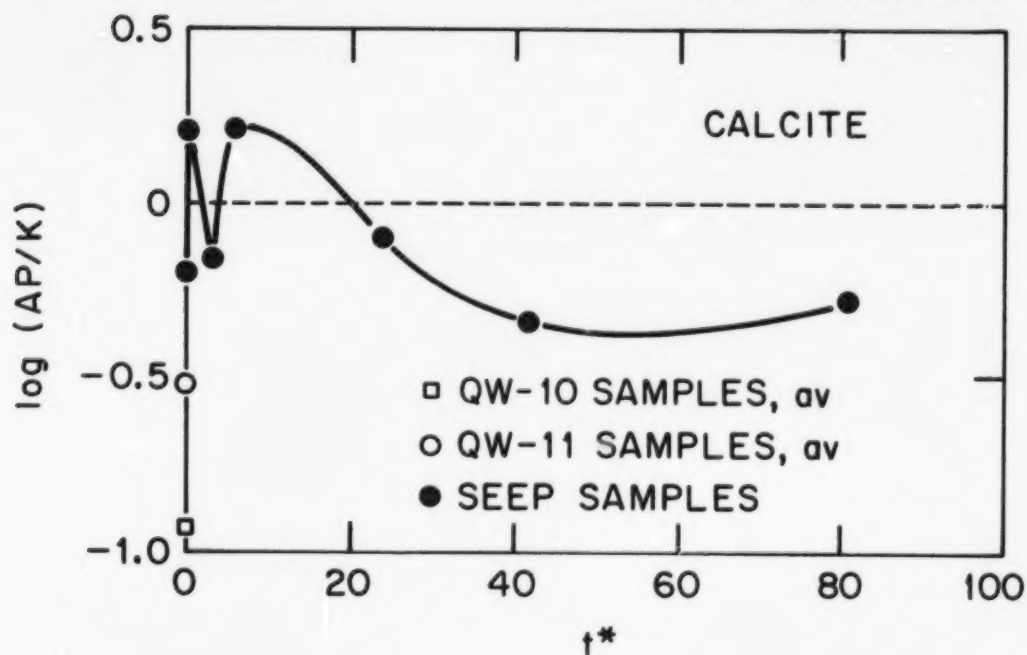


Fig. 8. pH, total carbonate, and silica concentration versus t^* (relative contact time) for water samples listed in Table 6.

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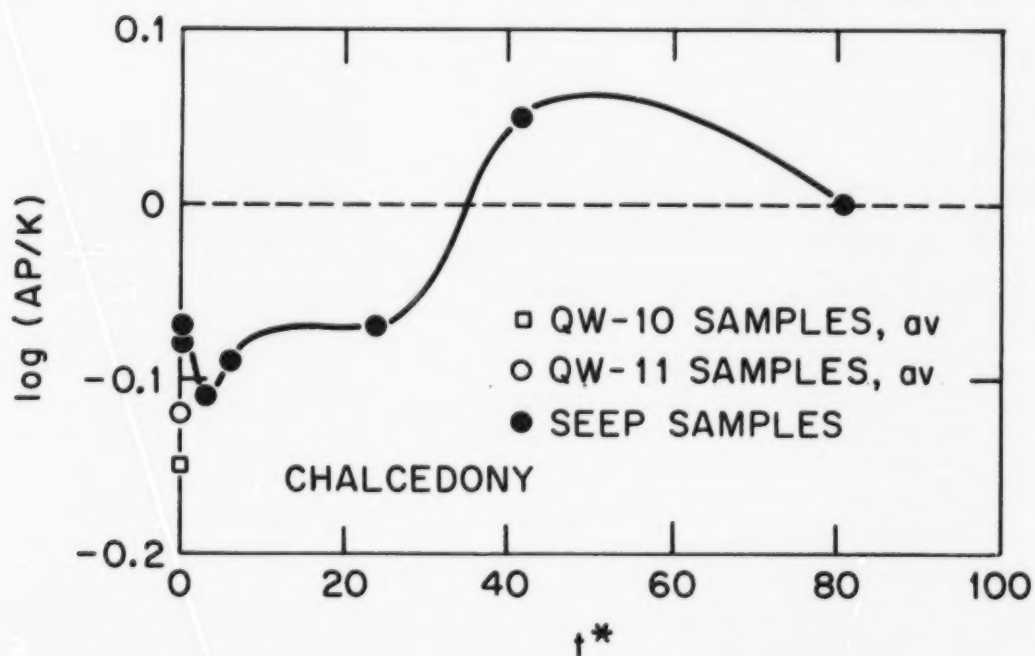


Fig. 9. Saturation indices ($\log AP/K$) for calcite and chalcedony as a function of t^* (relative contact time) for water samples listed in Table 6.

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The data are also consistent with an alternative interpretation of control of calcium and total carbonate by calcite solubility constraints alone. As pH increases as a result of the hydrolysis of silicates or CO₂ degassing, both calcium and total carbonate concentrations would decrease in order to maintain saturation with calcite. The hypothesis of Crisman and Jacobs (1982) that hydrolysis of silicates is responsible for the increase of pH is consistent with this interpretation. For example, the hydrolysis of albite would result in increased pH and an increase in the concentration of sodium, while calcium and total carbonate concentrations would decrease in response to calcite solubility constraints. However, the coupled ion exchange/calcite solubility mechanism discussed previously better accounts for all the chemistry data (e.g., sodium-calcium milliequivalent and t* relationships, total carbonate concentrations, and pH). Rather than validating or invalidating specific conclusions of Crisman and Jacobs, the fact that more than one mechanism is permissible to explain the relationships of the data emphasizes the importance of considering alternative conceptual models in interpreting groundwater chemistry data.

Crisman and Jacobs (1982) suggest that because changes in the water chemistry with distance into the MTUML adit (i.e., increasing overburden) are similar to changes with depth at the Hanford Site (e.g., increasing sodium and chlorine; decreasing calcium and total carbonate), even though mechanisms may be different, the chemistry of groundwaters in equilibrium with the two rocks might be similar. This hypothesis, however, has several problems. First, as was discussed earlier (see Sect. 7.3.1), the mechanisms controlling the chemistry of the groundwaters are probably quite different as a result of the mineralogical and textural differences between the two basalts, as well as the obvious difference between the source and age of the groundwaters. Second, although similar in some gross characteristics, the chemistry of the groundwaters from the MTUML and that at the Hanford Site are distinctly different. For example, the sodium and chlorine concentrations in the groundwaters within the Grande Ronde basalt are higher by a factor of ~10 than the highest concentration observed in the MTUML. The trend of sodium concentration with increasing t* (see Fig. 7) suggests that sodium concentrations would not continue to increase significantly in the groundwaters in the MTUML with increased contact time. Data from high-temperature rock/water experiments with Umtanum basalt and simulated groundwater from the Grande Ronde Formation (APTED 1982) suggests that sodium and chlorine may be considered as conservative elements and are not controlled by basalt/water interactions — in contradiction to the conclusions of Crisman and Jacobs. Early (1984b) has also suggested ion exchange as a possible mechanism for the control of sodium and calcium concentrations in some near-surface, Na/Ca-HCO₃-type groundwaters at Hanford (e.g., within the Saddle Mountains basalt), but that deeper, sodium-chlorine-type waters (e.g., within the Grande Ronde basalt) may have mixing with a saline ground-water as the source for the elevated levels of sodium and chlorine found in these waters. Based on the existing data and interpretations, the similarity between the chemistry of the groundwaters from the MTUML and those at the Hanford Site cannot be demonstrated with certainty to be a result of similar mechanisms, or to provide a sufficient basis for the assumption of analogous geochemical conditions relevant to the stability of copper in the basalts at the Hanford Site.

Redox Conditions and pH: As Crisman and Jacobs discuss, the pH and redox conditions (Eh) are two of the primary variables affecting the stability of copper in any geologic environment. For the analogy between the basalt/groundwater system in Michigan and that at the Hanford Site to be valid, evidence documenting some degree of similarity between the pH and redox conditions in the two systems is essential.

The pH of groundwaters in the Grande Ronde Formation at the Hanford Site has been measured and found to range from approximately 9 to 10 at 60°C (JACOBS 1981, EARLY 1984a). APTED and Myers (APTED 1982) suggest that at low temperatures the silicic acid buffer is the dominant control on pH, with carbonate equilibria being subordinate. The pH of the groundwaters in Michigan ranges from approximately 7 to 8.7, with the pH increasing with increasing overburden and relative contact time. Carbonate equilibria are the primary solution buffer. Although the range of pH values and mechanisms controlling pH are different in the two basalt/water systems, the analogy of native copper stability may still be valid, providing that interactions in the two basalt/water systems can be shown to result in redox conditions that, when coupled with the appropriate pH values, encompass the stability field of native copper.

Significant uncertainties are associated with determining the redox conditions in any low-temperature rock/water system. These problems stem from difficulties in the measurement, and concept, of Eh [LINDBERGH 1984 (and references therein)]. Because of the difficulties in measuring accurate values for Eh, indirect indicators of the redox potential of rock/water systems are useful to complement the use of platinum electrodes. Measurement of the dissolved oxygen content of groundwaters provides an excellent first indication as to whether the waters are highly oxidizing or not. Establishing the ratios of aqueous and/or dissolved gas redox couples (e.g., $\text{Fe}^{2+}/\text{Fe}^{3+}$, CO_2/CH_4 , $\text{SO}_4^{2-}/\text{HS}^-$) can provide additional indications of Eh, as well as allowing an evaluation of the state of equilibrium among the redox couples within the groundwater (LINDBERGH 1984). It must be remembered, however, that kinetic constraints may allow certain species to persist metastably outside their thermodynamic stability field [sulfate/sulfide equilibria are particularly prone to this problem (OHMOTO 1982)]. Mineral assemblages sensitive to redox potential can also provide an indirect indication of redox conditions for a rock/water system. As with the aqueous redox couples, information on several solids within a system can allow an evaluation of the state of equilibrium among the solids and the groundwater. It should be remembered that an indication of equilibrium does not always mean that the solids are controlling the redox potential of the solution, because another mechanism may be involved that allows the solids to precipitate under equilibrium conditions. Generally, the use of aqueous and solid redox couples works best at elevated temperatures, where equilibrium conditions are more prevalent (SEWARD 1974, ARNORSSON 1982).

The Eh within the Grande Ronde Formation at the Hanford Site has been proposed to be -0.45 ± 0.05 V (JACOBS 1981). This value is based on a model of dissolution of an Fe(II)-bearing glass and subsequent oxidation of aqueous Fe^{2+} to Fe^{3+} , resulting in the precipitation of iron oxides/hydroxides. Evidence to support the existence of these redox conditions includes mineral assemblages present within the Grande Ronde Formation

(pyrite, magnetite, general absence of hematite) and the ratios of dissolved gases (CO_2/CH_4) and aqueous species ($\text{SO}_4^{2-}/\text{HS}^-$). However, measured Eh values are consistently higher (+0.35 to -0.2 V, EARLY 1984a). Jantzen (1983) has shown in laboratory experiments that Grande Ronde basalt will react at 70°C with distilled, deionized water to yield a measured Eh of approximately -0.4 V, consistent with the proposed theoretical model of Jacobs and Apted (1981). However, an Eh value of approximately -0.1 V results when a simulated basaltic groundwater is used in the experiments. Lane et al. (1984) have shown that crushed basalt consumes dissolved oxygen rapidly at elevated temperatures. Therefore, even with the uncertainty associated with the measurement of Eh, and the problem of disequilibrium at low temperatures, the preponderance of the available field and laboratory data suggest that conditions in the basalt/water system at the Hanford Site are "reducing" compared to air-saturated or surface waters. However, the data do not demonstrate conclusively that the mechanism proposed by Jacobs and Apted (1981), or any other mechanism, is controlling the potential in the basalt/groundwater system at the Hanford Site to a value as low as -0.45 V.

Crisman and Jacobs assume that the Eh of the basalt/water system in Michigan is within the range +0.01 to -0.2 V (CRISMAN 1982, Fig. 26). This estimate is based solely on the coexistence of native copper and hematite. Crisman and Jacobs assume that the basalt provides an effective control for redox potential and that the apparent stability of the native copper-hematite assemblage reflects this control. As discussed earlier, two potential problems arise with an assumption such as this. First, the solid phases present in the rock may not be in equilibrium with the groundwater, which may itself contain several redox couples in disequilibrium and not possess a "single master Eh" (LINDBERGH 1984). Second, groundwater interactions with the native copper-hematite assemblage (or some other unidentified mechanism) may be controlling the redox potential of the groundwater and not basalt/water interactions. With the data available, it is not possible to identify the actual mechanism controlling the redox potential of the basalt/water system. However, the assumption of Crisman and Jacobs that the solid phases native copper and hematite are in equilibrium with the groundwater, and therefore a viable indicator of the redox potential of the groundwater, can be evaluated in an indirect manner.

We modeled the groundwaters with the geochemical code MINTEQ (FELMY 1984) for possible solubility controls on the reported concentrations of copper and iron (see Table 6). In an analysis similar to that presented by Deutsch et al. (1982), the saturation indices (SI) for native copper and selected iron-bearing phases were calculated as a function of $\text{pe} + \text{pH}$. For a given phase, it is permissible to interpret that the groundwater and the phase of interest are in equilibrium at the $\text{pe} + \text{pH}$ at which $\text{SI} = 0$. However, a result of $\text{SI} = 0$ is not unequivocal proof that equilibrium has been established, because other mechanisms may be influencing the concentration in solution with the fortuitous result that makes it appear that solubility control by the solid of interest controls the concentration in solution. If, as Crisman and Jacobs suggest, the coexistence of native copper and hematite indicates the Eh of the basalt/water system, then an identical value for $\text{pe} + \text{pH}$ should result at the condition $\text{SI} = 0.0$ calculated for native copper and hematite to be permissible solubility controls for copper and iron, respectively.

In addition to native copper and hematite, the iron-bearing phases, ferrihydrite and amorphous ferric hydroxide, were also modeled. Ferrihydrite and amorphous ferric hydroxide, although not identified as occurring in the Portage Lake Volcanics, are two phases commonly thought to be possible controls of the concentration of iron in groundwaters (DEUTSCH 1982) and were therefore included in the analysis.

Figure 10 illustrates the results of the calculations. Table 8 lists the values of $pe + pH$ that are required for each of the selected phases to be permissible solubility controls. The Eh values were calculated assuming a pH of 8.4 (the average for the seven seep samples within the MTUML). It is apparent that native copper is a plausible solubility control for copper if a value of approximately 9 is assumed for $pe + pH$. The Eh calculated for these conditions (+0.05 V) is in agreement with that proposed by Crisman and Jacobs (1982). However, Crisman and Jacobs proposed the Eh based on the coexistence of native copper and hematite. For hematite to be a permissible solubility control for iron, the Eh of the groundwater would have to be approximately -0.44 V. The only iron-bearing phase that could be a solubility control for iron and still be relatively consistent with an Eh for the stability of native copper is ferrihydrite. This phase has not been identified in the Portage Lake Volcanics.

The data and calculations involving redox-sensitive solids suggest that redox conditions in the groundwaters of the MTUML are probably reducing and may have Eh values ranging from approximately +0.1 to -0.5 V. However, without additional data (e.g., platinum electrode measurements, aqueous redox couples, etc.) and a sensitivity analysis to evaluate the effect of analytical uncertainties in the copper and iron concentrations, higher values for Eh cannot be ruled out. These results suggest that a single "master Eh" (LINDBERGH 1984) does not exist in the rock/water system of the MTUML and that the system is probably in a state of redox disequilibrium.

The redox conditions, and the mechanisms controlling them, are uncertain within the rock/water system in Michigan because of the mixed potential between at least two redox indicators (copper and iron phases). It is likely that conditions in this system are reducing because of the persistence of native copper, but a precise numerical range cannot be defined. Thus, the assumption of analogous redox conditions between the systems in Michigan and the Hanford Site is not necessarily valid based on the available data — especially in light of the proposed model for redox control in the system at the Hanford Site (JACOBS 1981) and the textural and mineralogical characteristics of the basalts in Michigan. Because a glass phase is not present in the Portage Lake Volcanics, a different mechanism must be involved from that proposed by Jacobs and Apted (1981) for the basalts at the Hanford Site. Therefore, it would be fortuitous that copper would be stable in the basalts of the Hanford Site based only on the analogy of the occurrence of native copper in the basalts of Michigan. An independent analysis of the redox conditions and controls in the basalts at the Hanford Site and the implications to the stability of copper is required.

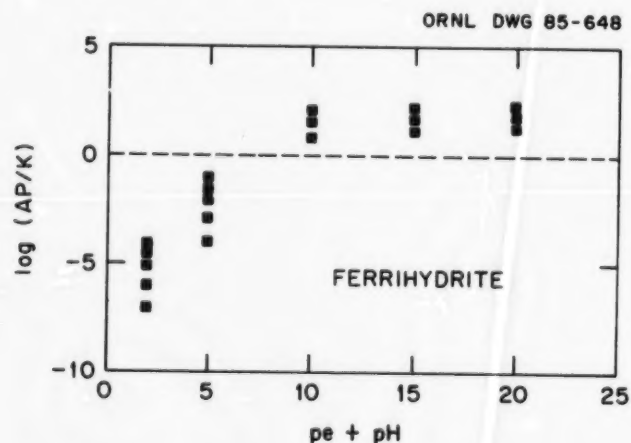
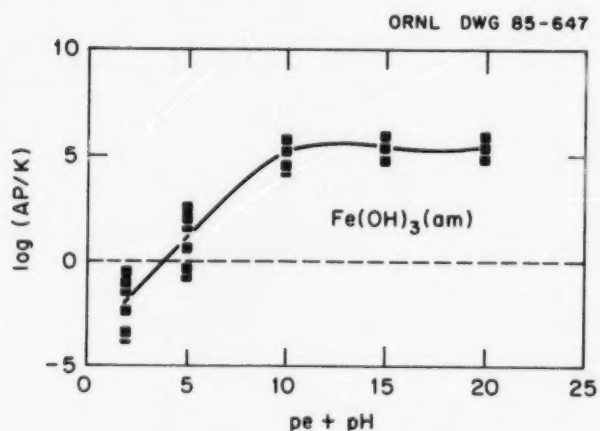
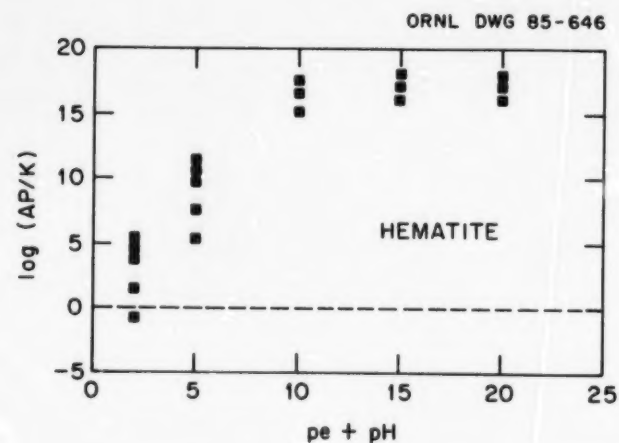
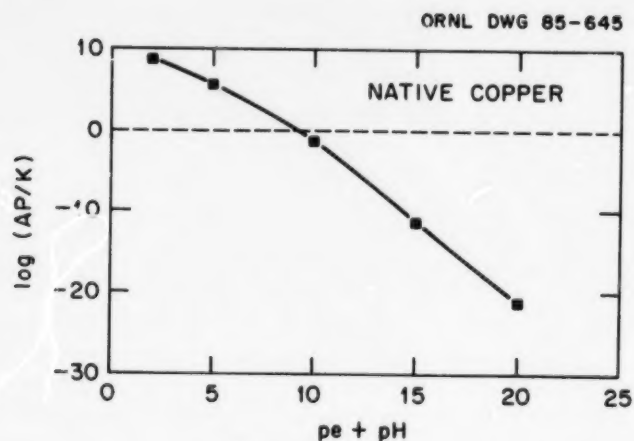


Fig. 10. Saturation indices (log AP/K) for native copper, hematite, amorphous ferric hydroxide, and ferrihydrite as a function of $pe + pH$. Each square represents the calculated saturation index at a given value of $pe + pH$ for the seep samples listed in Table 6.

Table 8. Values of $pe + pH$ and Eh necessary for selected phases to be permissible solubility controls for copper and iron^a [The values were calculated assuming $pH = 8.4$ (average of the seven seep samples from the MTUML)]

Phase	$pe + pH$ (at $SI = 0.0$)	Eh, V (at $SI = 0.0, pH = 8.4$)
Native copper	9.3	+0.05
Hematite	0.9	-0.44
Ferrihydrite	7.7	-0.04
Ferric hydroxide (am)	3.9	-0.27

^aFigure 10 of this work provides a calculated saturation index at a given value of $pe + pH$ for each seep sample.

7.4 CONCLUSIONS

The similarity in bulk chemistry of the basalts cannot be used to unequivocally conclude that similar geochemical conditions, and particularly controls on the geochemical conditions, exist with the two systems, because of the significant differences in the texture and mineralogy of the basalt occurrences in Michigan and at the Hanford Site. Better definition of the mechanisms involved in controlling the groundwater chemistry in the two systems is required before a valid analogy can be demonstrated.

The analysis of Crisman and Jacobs (1982) did not consider alternative conceptual models for the control of groundwater chemistry. Our evaluation has shown that mechanisms contributing to the control of water chemistry may have little relevance to basalt/water interactions. Rather, interactions with the glacial material and secondary minerals may be the predominant controls on the groundwater chemistry. The assumptions of Crisman and Jacobs concerning the "system Eh " of the basalt/groundwater system in Michigan have been shown to be incorrect. The system is probably in redox disequilibrium rather than equilibrium. At least two redox couples (copper and iron phases) are apparently out of equilibrium. The system is probably reducing, but precise numerical limits cannot be defined with the available data. Therefore, the conclusions of Crisman and Jacobs pertaining to the stability of native copper are tenuous at best.

The analysis of Crisman and Jacobs (1982) relied heavily on illustrating the similarity between the basalt chemistry and mineralogy, the groundwater chemistry, and the redox conditions between the rock/water system of the MTUML in Michigan and that at the Hanford Site. By analogy to the apparent stability of native copper in the basalts of Michigan, Crisman

and Jacobs concluded that copper may have favorable corrosion characteristics in the basalt/water system at the Hanford Site. Thus, should other candidate metals for the containment canister for high-level radioactive waste or spent fuel be found to have inadequate corrosion performance, copper may be a viable alternative. Crisman and Jacobs conclude that:

... copper alloys are very suitable materials as alternate canister materials for the emplacement in a nuclear waste repository located in basalt at the Hanford Site.

Our evaluation finds no firm evidence to disagree with this conclusion. In fact, based on the general characteristics of the two basalt/water systems, copper probably would be relatively stable in the basalts at the Hanford Site. However, our evaluation concludes that the analysis of Crisman and Jacobs alone is insufficient to demonstrate that a valid analogy exists which allows for direct conclusions to be made regarding the stability of copper in the proposed repository at the Hanford Site.

The native copper deposits in the Portage Lake Volcanics may be an excellent candidate for a more detailed study as a natural analog. The study, rather than attempting to reach conclusions pertaining to the absolute stability of copper as a containment canister material, should focus on the validation of mechanisms and parameters important to the long-term stability of native copper. The presence of native copper in contact with both fresh and saline groundwaters provides the opportunity to study copper stability under a variety of physicochemical conditions. In addition, the hydrologic setting of the MTUML might provide a unique opportunity to perform a field validation of groundwater flow models and geochemical models under controlled conditions where hydrologic parameters may be precisely determined and tracers used to monitor groundwater flow and geochemical reactions and transport.

8. ACKNOWLEDGEMENTS

The authors wish to acknowledge the excellent laboratory technical work performed by F. I. Case and G. C. Young, the secretarial effort of R. E. Dearien, and the editorial assistance of C. H. Shappert in the preparation of this document.

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2 TITLE AND SUBTITLE PROGRESS IN EVALUATION OF RADIONUCLIDE GEOCHEMICAL INFORMATION DEVELOPED BY DOE HIGH-LEVEL NUCLEAR WASTE REPOSITORY SITE PROJECTS: REPORT FOR OCTOBER - DECEMBER 1984									
5 AUTHOR(S) A. D. Kelmers, F. G. Seeley, W. D. Arnold, R. E. Meyer, G. K. Jacobs, and S. K. Whatley				4 DATE REPORT COMPLETED <table style="width: 100%; border: none;"> <tr> <td style="text-align: center; border: none;">MONTH</td> <td style="text-align: center; border: none;">YEAR</td> </tr> <tr> <td style="text-align: center; border: none;">April</td> <td style="text-align: center; border: none;">1985</td> </tr> </table>		MONTH	YEAR	April	1985
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10 SPONSORING ORGANIZATION NAME AND MAILING ADDRESS (Include Zip Code) Division of Waste Management Office of Nuclear Material Safety and Safeguards U.S. Nuclear Regulatory Commission Washington, DC 20555				8 PROJECT/TASK/WORK UNIT NUMBER 9 PIN OR GRANT NUMBER B0290					
12 SUPPLEMENTARY NOTES				11a TYPE OF REPORT Quarterly Progress Report b PERIOD COVERED (Inclusive dates) October-December 1984					
13 ABSTRACT (200 words or less) Geochemical information relevant to the retention of radionuclides by candidate high-level nuclear waste geologic repositories being characterized by Department of Energy (DOE) projects is being evaluated by Oak Ridge National Laboratory (ORNL) for the Nuclear Regulatory Commission (NRC). During this report period, emphasis was given to evaluation of published sorption and solubility information for key radionuclides which is relevant to the Hanford Site in the Columbia River basalts. The removal of neptunium from solution by basalt/groundwater systems under anoxic redox conditions at 60°C proved to be sensitive to the basalt particle size and the test contact time. It was not possible to establish if the neptunium removal from solution was due to sorption or precipitation processes. In studies of uranium solubility, sodium boltwoodite was shown to be the U(VI)-containing phase that precipitates from synthetic groundwater at 60°C. The precipitation of sodium boltwoodite, rather than schoepite which is predicted by geochemical modeling, shows the importance of identifying the solid phase in radionuclide experiments and highlights the weaknesses of the actinide thermodynamic data bases used in geochemical modeling calculations. An evaluation was made of the information developed by DOE on the native copper deposits of Michigan as a natural analog for the possible emplacement of copper canisters in a repository in basalt. The similarity in bulk chemistry of the basalts, relied upon heavily by DOE in their analysis, cannot be used to unequivocally conclude that similar geochemical controls, particularly controls on the geochemical conditions, exist within the basalt/water systems at Michigan and the Hanford Site. Thus, the DOE analysis is insufficient to conclude, with reasonable assurance, that copper will be stable at the Hanford Site.									
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